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Investigation of 3-D Fabrication of Ablative Materials

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Abstract

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Contacts with twenty five to thirty companies in the textile field have resulted in thirteen candidate specimens from outside vendors in house or on order covering sewing, needling, tufting, braiding, and multiple warp techniques. Inquiries on pile fabrics are in progress. Impregnation with epoxy resins has become routine and successful techniques with phenolics or epoxy phenolics appear imminent. Present mechanical test data (room temperature only) give the preliminary indication that these systems can be represented by anisotropic elasticity theory. The physical test matrix, specimen preparation, and thermal shock test design are also discussed in this report.

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I. Introduction

This program was initiated to evaluate methods of making a three-dimensional reinforcement, which will not have planes of weakness, to demonstrate the properties of composites made from these reinforcements and to select one or more methods for further effort.

The objectives of the first quarter were to:

1. Investigate methods of three dimensional fabric construction including definition of problem areas in such a construction.
2. Investigate methods of composite preparation.
3. Initiate acquisition of test data on impregnated samples.

This quarterly progress report summarizes the studies conducted to fulfill these objectives.

II. Technical Discussion

A. Fabric Studies

1. Avco Method 3-D Fabrics

The Avco fabric is constructed of straight non-interlaced yarns oriented in 3 orthogonal directions. This construction should optimize the interlaminar strength since straight yarns under pure tension are the reinforcement in this direction. Reinforcement density and stiffness in each direction can be varied independently by varying yarn size, density and material and additional reinforcement is possible in the 45^o directions of the X-Y plane. Yarn densities as high as 2000 yarns per square inch in any or all of the three directions are possible. Figures 1 and 2 are photographs of a typical sample of Avco fabric. Present practice standardizes these samples at 3" x 3" x 4" for proper physical testing in all directions. The loom on which these samples are woven is shown in Figure 3. Optimum utilization of this geometry requires close control over fabric compression or tightness and a superior impregnation technique. This latter is true because complete wet out of all reinforcement surface and good adhesion is necessary for efficient load transfer from reinforcement to matrix. If this load transfer does not occur the fibers in the direction of the stress will pull out of the matrix unlike most fabrics in which the reinforcement is locked in place by loops, knots or weaving.

The distribution ofyarn groups is unbalanced with regard to the X, Y and Z directions in the samples made to date. A modification of the loom has been made which virtually eliminates this deficiency. This modification decreases the size of the Z direction yarns but increases density four times by halving the spacing in the X-Y plane. Thus the pockets of unreinforced resin will be one fourth the present size despite identical overall bulk density.

Another step towards isotropic reinforcement is being studied through addition of yarns in the 45^o direction of the X-Y plane. With this variation in reinforcement available, the influence of reinforcement anisotropy on the ultimate tensile strength and modulus can be investigated more thoroughly. This allows the possibility of designing a fabric structure for specific mechanical strength which varies as needed with direction of stress. The modified loom for this weaving is pictured in Figure 4.

Considerable effort has been spent on design of a loom capable of weaving larger fabrics on a continuous basis. Although no construction has been done to date the conclusions are that such a machine is feasible in time, money, and operation and could produce virtually any width and depth of fabric in a continuous length.

Design effort has also been aimed at methods and equipment for producing cylindrical geometry which would be almost ideally suited for rocket nozzle applications. The construction studied would incorporate continuous circumferential yarns with consequent improvement in hoop strength. The other yarns would be axial and radial again giving an orthogonal construction. Continuous operation with large wall thicknesses appears more difficult than for the previously discussed structures but not impossible.

Five test pieces have been woven on the unmodified loom for impregnation studies and determination of physical properties. Test results on two samples are available and are described in the mechanical test section of this report.

2. "Modified State-of-the-Art Fabrics"

Since all of the other three dimensional fabrics under study, except braided and needled materials, are woven in a more conventional sense, a brief description of this process will be next, followed in more detail by the specific problems and findings on each method.

All weaving is essentially an interlacing of two sets of yarns and thus almost all looms are similar in their essential parts and corresponding mechanical action. The following description of the operation of the loom is presented in order to point out some of the specific difficulties which will be encountered in the fabrication of 3-D fabrics.

There are three primary motions on all looms: The dividing of the warp ends (longitudinal yarns) into two groups, known as "Shedding", the passage of the shuttle containing the filling (Lateral yarns) through this opening across the cloth, known as "Picking", and the pushing of the loose filling pick up next to the previous filling pick to form the cloth, known as "Beating-up". In addition to these primary motions, there are two secondary or contributing motions. The Let-Off Motion, warp yarn is fed into the loom, and the Take-up Motion, which controls the rate at which the completed cloth is taken away.

For looms of any type to function properly under power, each of these motions must be automatically synchronized, so that they work in harmony.

1. Shedding motion - This motion consists of the separation of all warp yarns into two groups to permit the shuttle to pass through the resulting shed. For some complicated weaves, such as the 3-D, an attachment known as the Jacquard Head could be used. This equipment allows every warp thread to be controlled independently to produce the desired shedding action. Present loom designs limit the size of the shed when weaving very thick fabrics and hence would impose a thickness limitation on the resulting fabric. The actual thickness of the fabric that could be achieved would have to be determined experimentally and would also be a function of the size of the yarns.

2. Picking motion - When the shed is formed, the shuttle (carrying the filling) is propelled across the loom through the warp. This is referred to as the picking motion. As the thickness of the fabric is built up, the position of the shed is raised, requiring the path of the shuttle also to be raised. In the powered operation, this adjustment requires a modification of the equipment, but for the fabrication of initial samples, this motion may be successfully accomplished by hand for the entire thickness of fabric.

3. Beating-up motion - Consists of pushing the filling pick into the cloth by means of a reed (comb). Where several filling yarns are in a vertical line with each other, some machine adjustments may have to be made in order for yarns to be struck simultaneously.

a. Multiple Warp

A material having a cross-section similar to that in Figure 5 may potentially be developed by the multiple warp principle of weaving. In this geometry, warp yarns (longitudinal) of each fabric layer are mechanically interlocked with the filling yarns of the adjacent layer to produce strength in the direction perpendicular to the surface of the material (radial). If requirements should demand, each layer may be interlocked with layers deeper in the material instead of, or in addition to, the adjacent layers. Thus it is seen that the yarns joining each layer in the radial direction form an integral part with the reinforcing yarns in the longitudinal and transverse directions. This geometric feature is desirable from the viewpoint that the transmission of loads from ply to ply does not depend exclusively on the properties of the laminating resin but is dependent on the mechanical integrity of the reinforcing material itself. The advantage of this geometry under ablation conditions when the resin is decomposed is obvious.

Multiple warp structures consisting of three to four layers of fabric each interlaced with adjacent layers can currently be fabricated on conventional tensile looms. Thicknesses can range from 0.080 to 0.250 inches depending upon the size of the yarn. It is felt that the weaving process can be extended to fabricate materials having thicknesses in excess of one inch.

Although considerable changes may have to be made in the design of the equipment to produce a 3-D fabric continuously under power, the fabrication of preliminary samples may well be accomplished by operating the loom motions by hand with only minor machine adjustments.

Dobby looms having 28 harnesses are readily available and are capable theoretically of weaving up to fourteen fabric layers. The chances of achieving a 0.500 inch thick fabric are considered good.

If the initial samples hand woven on such a Dobby loom are successful, the same weaving principles can be applied to achieve large fabric thicknesses (possibly in the order of five inches) on a three-position Jacquard-head loom. This equipment is available in the textile industry; it has the ability to control as many as 1200 warp yarns independent of each other. It essentially acts as 1200 harness loom.

Five companies have shown an initial interest in supplying multiwarp fabrics of glass. They are:

Raypan Development Industries, Huntington Park, California
J.P. Stevens and Company, Inc., New York, New York
Prodesco Company, Perkasie, Pennsylvania
Callaway Mills Company, LaGrange, Georgia
Bigelow-Sanford Carpet Company, Thomsonville, Connecticut

However initial confidence in this capability has not been born out in all cases. Raypan supplied a 3" thick sample made up by hand sewing 1/4" thick multiple warp fabric layers together as shown in Figures 6 and 7. J.P. Stevens' multiple warp sample, only 1/4" thick, was made by a combination of weaving and knitting process. Figures 8 and 9 show the J.P. Stevens fabric. Only the Raypan sample was large enough to permit more than a preliminary examination. A larger sample of the J.P. Stevens fabric is on order due in this week.

Specific problems encountered so far in multiple warp weaving are tied in with yarn size desired and in automation. Finer yarns decrease the resin pocket size and improve the eveness of ablation but this means more warps to produce a given thickness. As stated before, even large machines have space and handling capacity for a finite number of warps e.g. even 1200 warps at 20 picks per inch will give only 3 square inches, say 1" x 3", of fabric cross-section. Automation of the picking motion, weaving the fill threads, for a twenty warp thickness would require the warp yarns to move vertically to accommodate nineteen shuttles simultaneously or in rapid succession. Most looms do not have this vertical height available. This could be accomplished by hand but the weaving process would be extremely slow. Many of the looms that handle the finer yarns readily are not stiff enough to beat up (compact) the large number of fill threads during weaving. Several companies are reluctant to weave glass because of its abrasive properties and the large cleanup time required for equipment turnaround.

Preliminary estimates of cost and time to develop the ideas discussed with several of these companies range from 6 to 9 months in time and $100,000 - 250,000. This would consist of major modification or redesign of present machinery but would be capable of weaving fabrics in the range of three to five inches thick and twelve inches wide.

b. Multiple Fabric Layer Sewing

Two samples have been obtained of multiple layers of fabric sewn together with 15 to 30 threads per square inch. The machine sewn sample, $\sim \frac{1}{2}$" thick, had very poor fabric integrity since the relative motion of the fabric and needle caused tearing to occur. The thread used in this attempt also broke unduly due to brittleness. Hand sewing maintained the fabric integrity but thread brittleness required retying every two or three stitches. Figure 10 and 11 illustrate the hand sewn sample from H. Harwood and Sons, Inc., Natick, Mass. This method would be improved by using Teflon* coated thread but would still be very slow and limited to about 1-$1\frac{1}{2}$" thickness. A substantial improvement might be obtained by employing a multiple needle sewing machine with the Teflon* coated thread to sew through a carefully placed stack i.e. good registration, of an open weave e.g. leno weave cloth. At its best sewing does not appear as practical a solution as some of the other methods described in this report.

c. Braiding

Braiding is essentially a technique for weaving in a cylindrical shape. Figure 12 shows a typical normal braid supplied in glass by Valrayco of Pawtucket, Rhode Island which will be used as the control material for the interlocked braid to be supplied by the same company. Figure 13 is a photograph of a typical braiding machine. This sample is composed of layers of helically wound and interlocked yarns, one layer on top of another but with no interlock occurring between one layer and the next.

This company is currently making a braided sample for Avco which will contain an interlock between all layers at every point of intersection of the helically wound yarns. Figure 14 is a photograph of a smaller sample showing three interlocking techniques. The sample on order will use either type 1 or 3 interlocks. The finer the helical yarns, the closer together can be their intersections, and consequently the more numerous can be the layer to layer interlocks in the axial direction. The number of interlocks around a circumference is limited by the machine and/or inside diameter of

*duPont trademark

the tube. For this reason, this sample will contain the finest yarns helically which are consistent with practical machine operation. This sample will have 12 interlocks per circumference which is the particular machine capacity though other machines can make up to 96 interlocks per circumference. If the ratio of O.D. to I.D. desired is too large, a braided fabric would have to be started on a small machine which would limit circumferential interlocks and then be moved to a larger machine to bring it up to final O.D. if circumferential interlocks per inch were to be held as constant as possible.

The sample containing the layer to layer interlocks will be tested in a composite form and its properties compared to the braided non-interlocked control sample.

This process is considered the most adaptable of all these being considered as far as large cylindrical shapes are concerned. That is, if shown to be capable of producing samples with good 3-D properties, this process could probably produce large, cylindrical shapes with the least machine modification and least cost involved of any of the processes being considered at the present time.

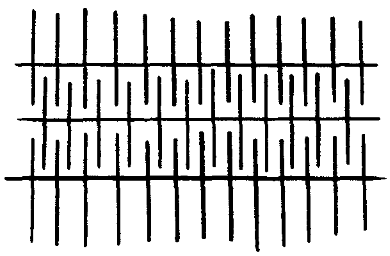
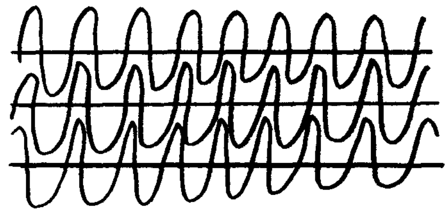
d. Tufted Fabrics

Tufted fabrics are pile fabrics made by sewing loops of fibers through an already woven backing cloth or web. Figure 15 and 16 show the tufting process and the loop length control. A high density fabric can be made by a minor modification of this process. If multiple layers of cloth are fed to the machine it acts as a multi needle sewing machine without a binding thread for the stitches. Present machinery allows tufting through ten to fourteen layers of fabric. Control of fiber density in such a construction is made by selection of tufting thread diameter, spacing of the needles and weave of the backing cloth. Some looseness is inherent in the fabric since openings in the backing cloth must accommodate both the needles and the tufting thread and no beating up motion (compaction) is made in the machine.

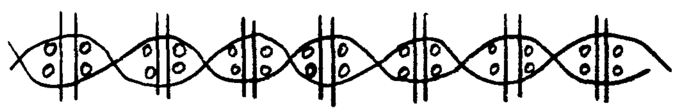
J.P. Stevens has made a sample for Avco with 64 tufts/square inch through fourteen layers which is in the heat cleaning stage. Machine modifications can increase the tufting density but a compromise is mandatory since larger needles are required for stiffness in penetrating the desired layers of fabric while thinner needles permit tighter construction and closer yarn spacing with finer yarns. Another problem in tufting which gets progressively worse as the number of layers increases and the needle spacing decreases is the registration of the holes in the fabric. This is necessary for easier needle penetration and minimized fabric break up during tufting. A leno type weave for the backing cloth with a minimum of thread displacement under handling could minimize this problem.

e. Pile and Loop Fabrics

Pile or loop fabrics, in contrast to tufted fabrics, have the loop or pile woven into the fabric as shown in Figures 17 and 18 respectively. Double pile or loop fabrics have the potential to interlock with each succeeding layer according to the sketches below.

Several manufacturers of loop or pile fabrics have been contacted. However only two have signified an interest in working on a double pile fabric in glass. Lowell Technological Institute has been attempting fabrication of a pile fabric with only partial success to date. Schlegel Manufacturing Company, Rochester, N.Y. is attempting to produce a double pile fabric in glass. Results should be available next month. Bigelow-Sanford Company, Thompsonville, Conn. can presently make double pile fabrics of the following structure:



Since the pile is only held together by inter fiber friction which is very low in the smooth skinned glass, the consensus was that glass fibers would not work in this process on this loom. The problem is concentrated in holding the pile fibers during the beating up of the fabric. Efforts are continuing to obtain a double pile or its easier counter part a double loop fabric.

f. Needled Felts and Fabric-Felts

Needling involves forcing matt fibers into and through itself in a plane perpendicular to its surface with barbed needles as shown in Figure 19. This process is used in making felts as shown in Figure 20. This technique can be employed with alternating layers of fabric and matt, the combination of which has much superior tensile properties in the plane of the fabric than does a pure felt. If the needles continue into a piece of fabric, than the matt is mechanically linked to the fabric by hundreds of small fibers. This method does damage the fabric due to the tearing action of the needle barbs.

Figures 21 and 22 show a needled sample obtained through Henry Simonds an Avco consultant. This will be characterized in addition to a series of six samples from J.P. Stevens Company made with three needling depths and two needling densities at each depth. These variations should determine the effect of the degree of vertical orientation on interlaminar strength and the degree of fabric damage.

B. Resin Impregnation and Composite Studies

1. General

The current processing techniques employed in the production of fiberglass fabric reinforced plastics are the result of years of effort and the state-of-the-art has advanced greatly since the introduction of automated processing equipment for producing uniform pre-impregnated fabrics. The quality of the laminated materials produced however, are largely influenced by the selection of pre-impregnated fabric characteristics, molding conditions, and techniques employed in the processing of the materials. As a result the mechanical properties of laminates vary widely from part to part, especially when purchased from different sources.

The most critical property in any laminated structure that contributes to premature mechanical failure especially under thermal shock is its inherently weak interlaminar tensile or shear strength.

The automated techniques usually employed in applying and B-staging resins to prepare preimpregnated reinforcement cannot be used for the 3-D materials because of restrictions inherent in their size and shape.

The overall objective of this phase of the program is to develop a resin impregnation technique employing epoxy and/or phenolic resin as the impregnant for 3-D woven structures. The method that is developed must be suitable for impregnating most of the 3-D woven materials being considered throughout the program. The criteria for the selection of a satisfactory method and resin are primarily based on achieving a final density (1.90 - 2.00 g/cc), volume porosity (less than 5% - air pycnometer) and resin content (28-32%) values on impregnated material equivalent to those obtained for high quality fiberglass laminates.

Of the two classes of resins being considered, the phenolics are much more difficult to process due to the inherent release of volatiles during cure yet this is offset by the thermal stability of this type of resin. Both classes of resins are being pursued however, so that any significant advantages in processing or final material properties found in either resin system may be exploited.

In order to expedite the program efforts and because of the high cost of the 3-D woven structures for experimental study 181 fiberglass fabric was used for the initial impregnation studies. The fabric used in all experiments was compressed dry to a predetermined density (1.35 to 1.40 g/cc) and held secure in a simple clamping fixture to simulate the density of the 3-D woven structures being produced.

2. Epoxy Resin Impregnation Studies

a. Avco 3-D

A technique for impregnating Avco 3-D fiberglass structures with epoxy resins has been worked out. The technique consists of encapsulating the lateral sides of the 3-D structure with silicone rubber (RTV-60) about 3" from the bottom of a 4" dia. x 18" long steel tube thus leaving the top and bottom of the structure open. The epoxy resin system - Araldite 6005/Epon 872/$BF_3$400 is mixed hot and poured in the longest open end of the tube such that it rests on the top open end of the 3-D structure. Vacuum is then applied at the short end of the tube and a piston is placed at the longest end to force the resin through the 3-D structure while the vacuum is on. As soon as resin appears at the vacuum end, the vacuum is shut off and the piston pressure is released. Then the impregnated 3-D structure is allowed to cure for 16 hrs. @ 235°F, postcure for 5 hrs. @ 300°F and is then cooled to room temperature before removal from the tube.

Two Avco 3-D blocks (3" x 3" x 4") samples #19 and #26 and one block of Raypan Multiple-Warp fabric ($2\frac{1}{4}$ x $2\frac{1}{4}$ x 2 3/4") have been impregnated in this manner. The materials were sectioned for mechanical evaluation and results are reported in the testing section of this report.

b. Reference Materials

Two fiberglass-epoxy laminates (6" x 6" x 4") have been compression molded for evaluation of material properties. The laminates were prepared from 9 oz. fabric (18 x 18 construction, .011" thick, 150's filament size yarn-Volan finish) and an acetone solution of the standard epoxy resin system - Araldite 6005/Epon 872/$BF_3$400. The fabric was preimpregnated employing a manually operated lab impregnator equipped with rubber squeeze rolls.

The resin coated fabric panels were then B-staged in a large walk-in circulating air oven for 20 to 25 minutes @ 250°F plus 10-15 minutes @ 290°F.

The B-staged fabric panels were die cut (6" x 6") and placed in a vented mold for processing. A molding pressure of 800 psi was applied to debulk approximately 8" of material. The compressed material was cured for 4 hrs. @ 250°, 2 hrs. @ 275°, postcured 6 hrs. @ 300° and then cooled under pressure overnight.

After curing the laminates were trimmed and the resin content and density was calculated. Results were as follows:

Code No.	Resin Content, %	Density, g/cc
874-76	28.3	1.90
874-84	28.9	1.92

The laminates are presently being machined into test specimens for evaluation of mechanical properties and thermal shock characteristics. The properties obtained from this material will be used as the reference control throughout the program for comparison with other materials being evaluated.

The fabric construction employed to prepare these laminates was chosen because it is more representative of the construction used in Avco 3-D with regard to threads per square inch.

3. Vendor's 3-D Materials

It is anticipated that the 3-D fiberglass woven materials received from outside sources will be impregnated with the standard epoxy resin system. The specific construction of each of these materials is discussed in detail in the Fabric Studies portion of this report.

Attempts to develop an epoxy impregnation technique that is applicable to all of the various 3-D constructions is currently under investigation.

The purpose of this work is to find a technique that can be employed to maintain the final resin content of the 3-D materials in the range of 28-32%. The resin content needs to be controlled within this range, to allow a valid comparison with the reference control and Avco 3-D material.

4. Phenolic Resin Impregnation Studies

a. Phenolic Impregnations

Several approaches have been evaluated for the impregnation of 3-D structure with Monsanto SC1008 phenolic resin. Both clamped fabric and Avco 3-D structures were employed in the resin impregnation studies.

At the onset of the impregnation studies it was found that a resin specific gravity of 1.050 and viscosity of 25-50 cps (Brookfield) was required for complete impregnation. These conditions were achieved by simply heating the as received resin (sp. gr. - 1.075) to 150-180°F. However, as the resin ages in cold storage (30°F) it becomes necessary to dilute the resin with additional solvent (isopropanol) to achieve the desired resin characteristics for impregnation.

Most of the materials evaluated were initially treated accordingly. Samples were placed in 150-180°F phenolic resin. As the resin is heated solvent volatiles are slowly evolved without foaming of the resin. When the resin has reached a gelled condition, the residual volatile content was measured and in most cases was found to range between 15-20%. At this stage the impregnated parts were removed from the gelled resin bath for further processing.

The first group of samples were processed by soaking in 150-180°F resin for various periods of time then cured to 350°F with the aid of external pressure whereas the second group was gelled and processed without application of external pressure. In addition, one of the samples (#874-82) was treated with new high solids (75%) resin—Colab 397. Results of these experiments appear in Table I.

b. Phenolic/Epoxy Impregnations

Another approach used was to soak the material in resin for 4 hours at 150°F and then remove the impregnated part for drying at 180°F for 16 hours. The part was the cured from 200° to 350°F. This procedure was repeated three times and then the part was impregnated with low viscosity epoxy to fill the open porosity. Results for Avco 3-D sample #874-86 (41) employing this simplified technique is given in Table I. Another Avco 3-D sample (3" x 3" x 4") was impregnated using this procedure with the exception that a portion (1/3) of the material was sectioned for evaluation in the phenolic impregnated condition and the remaining portion (2/3) for evaluation in the phenolic/epoxy impregnated conditions. The materials are currently in the process of being sectioned for physical and mechanical property determination.

As a result of this new approach, portions of each material previously processed with phenolic were impregnated with the low viscosity epoxy resin to determine the effectiveness of the epoxy impregnation. Density, porosity, and resin content measurements taken on all materials after the phenolic and epoxy impregnations appear in Table II.

C. Testing

1. Mechanical

The latest available mechanical test data for two epoxy resin composites is presented in Tables III through X. Before discussing the results in detail, it should be noted that the Raypan 3-D sample was relatively non-uniform and the laminates were not fully parallel. This had the obvious effect of increasing the scatter of ultimate tensile strengths and moduli (See Table VIII). Another Raypan 3-D specimen is scheduled to be fabricated and tested.

A major effort in the mechanical testing area has been to determine whether or not the reinforced plastic systems under consideration could be represented according to anisotropic elasticity theory. On the basis of the available test data, the room temperature moduli variations can be predicted successfully with reasonable accuracy. Figure 23 is a comparison of calculated and observed modulus variation for the Avco/RAD 3-D epoxy and the material can be represented as an orthotropic medium where the moduli $E_1 = E_2 = E_3$, and the angular variation of the moduli E_1' in a rotated coordinate system may be calculated according to:

$$\frac{1}{E_1'} = \frac{\cos^4\phi}{E_1} + \left(\frac{1}{G_{12}} - \frac{2\nu_{12}}{E_1}\right)\sin^2\phi\cos^2\phi + \frac{\sin^4\phi}{E_2} \qquad (1.1)$$

with E_1, E_2 being the uniaxial moduli in the appropriate directions and
G_{12} = shear modulus
ν_{12} = Poisson's ratio

The modulus variation for the Raypan 3-D has not been predicted since sufficient data has not been obtained to characterize this transversely isotropic composite. In this reinforcement system the modulus transverse to the reinforcing direction is not equal to that parallel to the laminates and this will result in a continuously decreasing modulus rather than the characteristic curve shown for the Avco/RAD 3-D epoxy.

An attempt was also made to predict the ultimate strength variation in the X-Y plane for the Avco/RAD 3-D material. Applying the anisotropic yield criterion discussed by Hill, and more recently investigated by Tsai, for the case of plane stress, one obtains for angular variation of ultimate tensile strength

$$\sigma_x' = \frac{\sigma_x}{\sqrt{\cos^4\phi + \left[\left(\frac{\sigma_x}{\tau}\right)^2 - 1\right]\cos^2\phi\sin^2\phi + \frac{\sigma_x}{\sigma_y}\sin^4\phi}} \qquad (1.2)$$

where σ_x, σ_y = ultimate tensile strength in X, Y direction, τ_{max} = maximum shear stress. This formula is of interest since it indicates the controlling influence of the ratio of maximum shear stress and transverse strength to the maximum σ_x strength.

For most composites these ratios are considerably larger than for the Avco/RAD reinforcement scheme, with resulting larger angular variations in ultimate strengths as compared to the Avco material. One can easily see that the most favorable condition from the point of view of approaching a homogeneous, isotropic medium, is the case when τ maximum approaches the maximum σ_x strength and when $\sigma_x = \sigma_y$. Then there will be a minimum angular effect on the ultimate strengths. The formula has not been applied to all the materials considered since thus far, only relatively small blocks have been fabricated and not all of the requisite mechanical property data has been obtained from exactly similar samples. Larger specimens are to be fabricated and room temperature data will be available in the necessary directions in the next reporting period for selected materials.

Consideration of equations (1.1) and (1.2) as well as the fact that for an orthotropic material, the shear modulus variation can probably be represented by the formula

$$\frac{1}{G_{12}'} = 4\left(\frac{1}{E_1} + \frac{1}{E_2} + \frac{2\nu_{12}}{E_3} - \frac{1}{G_{12}}\right)\sin^2\phi\cos^2\phi + \frac{1}{G_{12}} \qquad (1.3)$$

which suggests the desirability of measuring the moduli E_1, E_2, G_{12} and ν_{12} as well as observation of the ultimate tensile, compressive and shear strengths in various directions. There is however, the obvious limitation of sample size to contend with, and several extreme cases must be considered, namely:

1) relatively thin laminates

2) tubular braided samples

Because, in general, shear strengths determined from quarter point loading flexure tests, core shear, or Jacob bar shear tests do not give the same results, it would be desirable to perform at least one series of similar tests on all the candidate materials so that the comparisons will be valid. Since it it probable that shear failures induced by compressive loads may differ appreciably from those induced by tensile loads, quarter point load flexure behavior is considerably influenced by beam span to depth ratios. On the other hand, simple core shear tests, because they involve crushing of the reinforcement, may not be advisable particularly when different reinforcing schemes are being studied. It is suggested that notched bar shear tests be used for determining shear strengths of the laminates and that notched ring specimens be used for thin cylindrical specimens. Normal notched bar tests will be used for high O.D./I.D. ratio braided tubular materials. Simple tension tests can be performed on slightly tapered butt tensile bars while the small rings can also serve for ultimate tensile strength determinations. The screening tests for the various candidate composites can probably consist merely of tensile tests in the strongest and weakest directions for the various materials and shear strength measurements across the weakest plane. Suggested sample designs are shown in Figure 24. The two most promising reinforced plastics may then be more completely characterized by tension, compression and torsion tests in several directions, at room temperature and at an elevated temperature.

2. Thermal Shock Tests

In order to select the rocket nozzle material on a more realistic basis, in addition to the mechanical properties test program, two types of thermal tests are to be conducted. Previously the Mechanical Evaluation Group has applied radio frequency dielectric heating techniques in order to rapidly raise the temperature of the test samples. Because conducting metals cannot be placed in the magnetic field, devising a thermal shock test is not a straight forward routine matter. For this and other reasons the existing Avco/RAD high temperature resistance heating facility is suggested for the thermal shock experimentation. The manner in which these tests will be performed is as follows:

1) Sharp thermal gradients will be imposed across the thickness of 3" x 3" x $\frac{1}{4}$" plates in order to induce interlaminar shear failures. The temperature profile will be achieved by placing one face of the plate against a thin tungsten sheet which has previously been raised to high temperature. Tests will be conducted to determine the conditions necessary to cause failure in typical laminates and in the prime candidate three dimensionally reinforced plastic system.

2) Tubular samples will be positioned over a solid cylindrical tungsten heating core and restrained axially between rigid load platens. By simultaneously restricting axial motion and rapidly heating the tungsten heating element, gross failures will be induced in the 3-D composites and comparison of the performance of the various materials can be made on the basis of observed temperature profiles and required restraining forces.

III. Financial Status

It is anticipated that the funds remaining are sufficient to complete the program requirements.

IV. Future Work Planned

Since representative samples have been obtained or are on order for most of the reinforcing techniques which were to be studied, emphasis in the fabric studies will shift from sample procurement to a detailed assessment of commercial practicability of these techniques. Primary emphasis in the impregnation area will be sample preparation for mechanical testing while the testing area will divide its effort between assuring the validity of the tests in the Physical Test Matrix and subsequently routine testing of the candidate composites.

Satisfactory samples from two of the more important ideas have not been obtained. Efforts will be made to obtain these two which are a thick (1" minimum) multiple warp sample through hand weaving and a double pile fabric. The now standardized impregnation with epoxy resin will continue on samples in house and on order as they are received. Contacts with industry will be maintained to improve our knowledge of the commercial practicability of the candidate weaving techniques.

Mechanical tests will be performed on selected samples in house to assess the validity of the tests prior to finalization and full sample entry into the test matrix. This will be done primarily for thin material and braided samples.

Phenolic impregnation studies will continue to determine the generality of the technique to Avco 3-D and other highly dense samples. This study will provide a charring resin composite which will allow evaluation of 3-D char properties. The now standard epoxy impregnation technique will be used to prepare the candidate fabrics for physical testing.

Visits are planned with Crompton and Knowles Corporation of Worcester and Huyk Corporation, Rennsalaer, N.Y.

The limited test data generated so far in this program corroborates the thesis that substantial improvement can be obtained in the interlaminar tensile and shear strength of fabric reinforced composites.

While this limited data does not spell out which reinforcing technique is the optimum further work towards utilization in commercial hardware is indicated. The areas of knowledge that need to be defined and are beyond the scope of this contract are:

1. Confirmation of the utility of increased interlaminar tensile and shear strength in a char and/or high shear ablation test.

2. Confirmation of the feasibility of machine development for fabrication of materials of the required dimensions.

3. Consideration of typical reinforcement materials, (refrasil, carbon) and/or promising more exotic materials in terms of fabricability and composite performance.

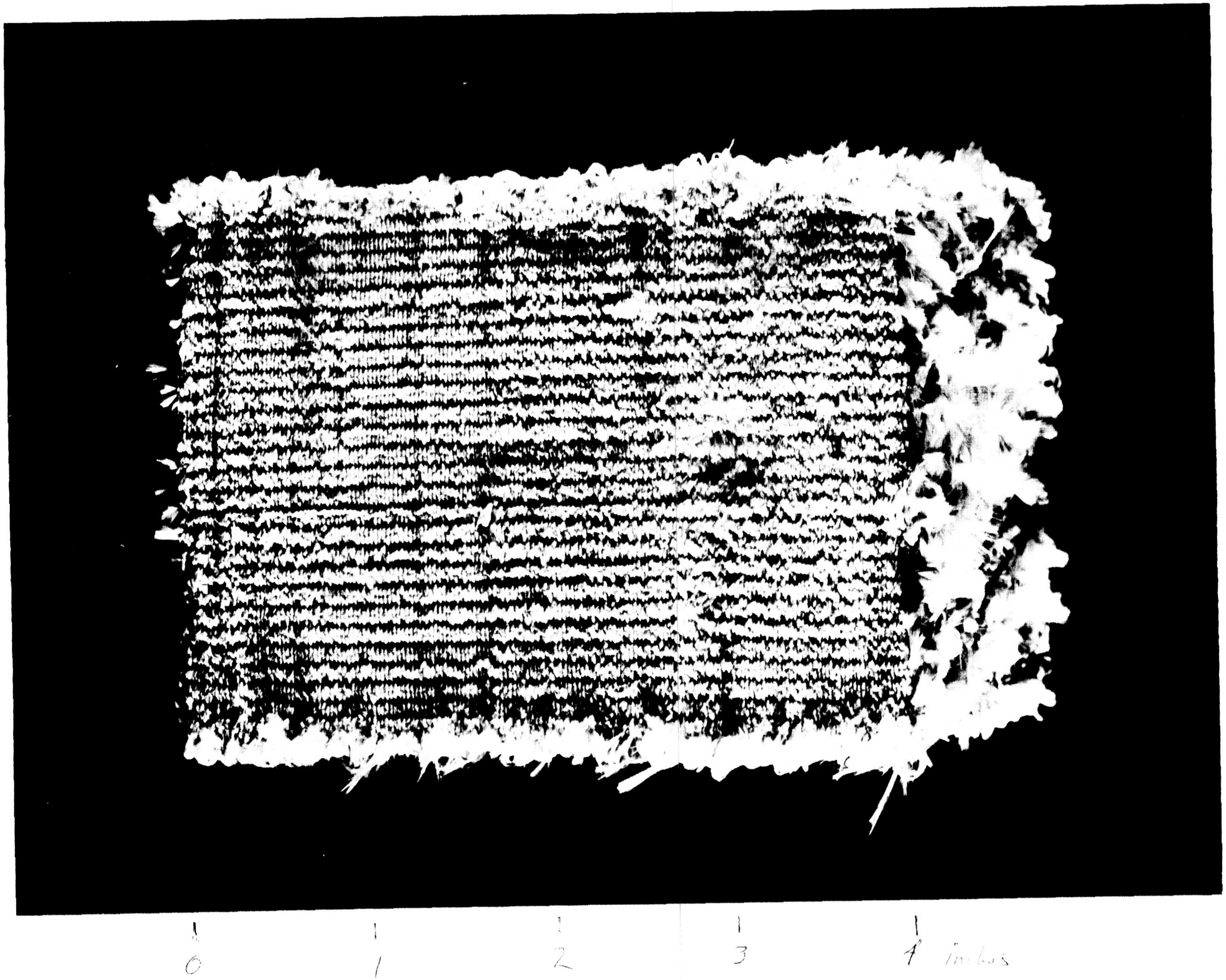


Fig. 1 Avco 3-D Y-Z Plane

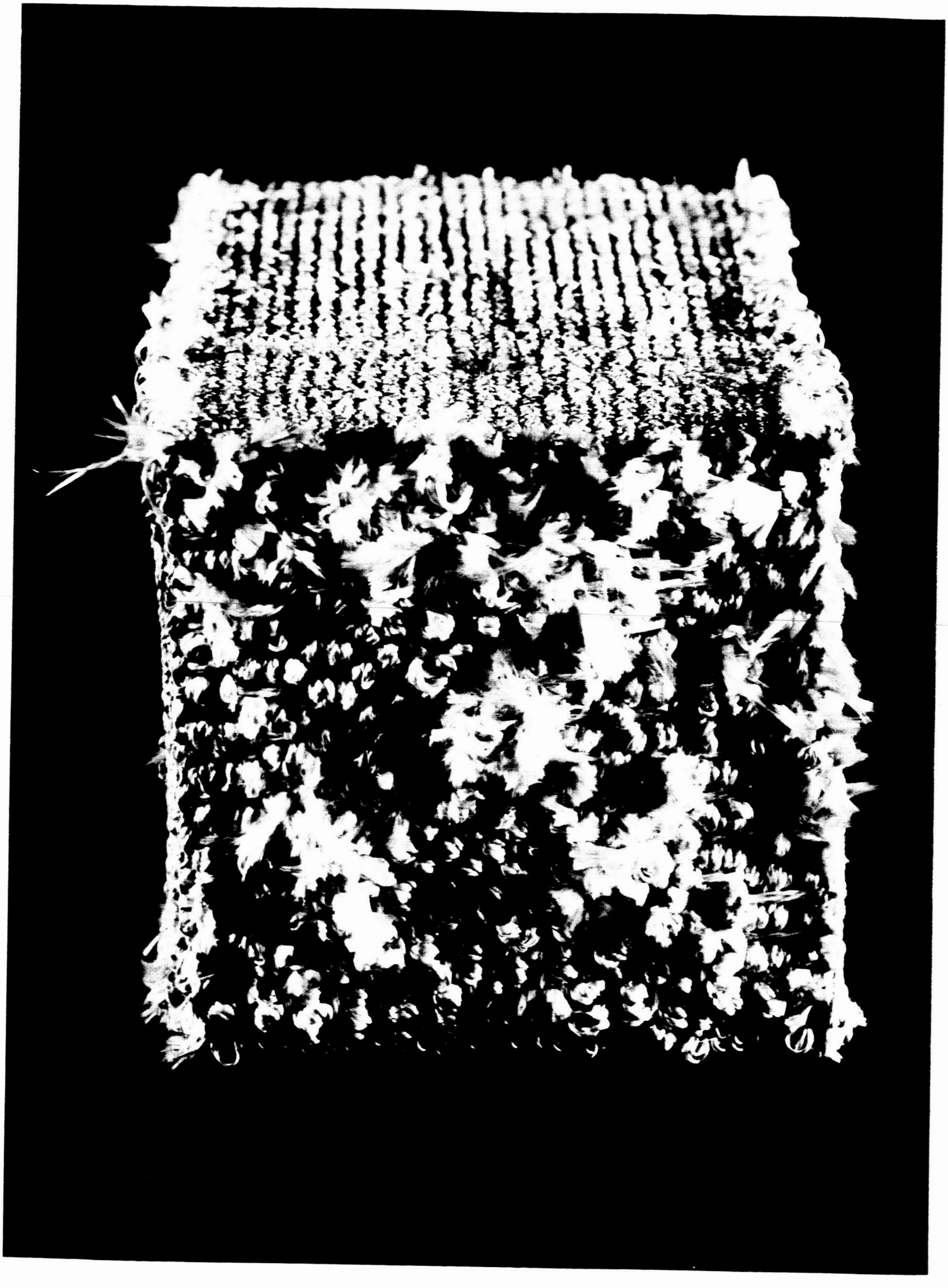


Fig. 2 Avco 3-D X-Y Plane

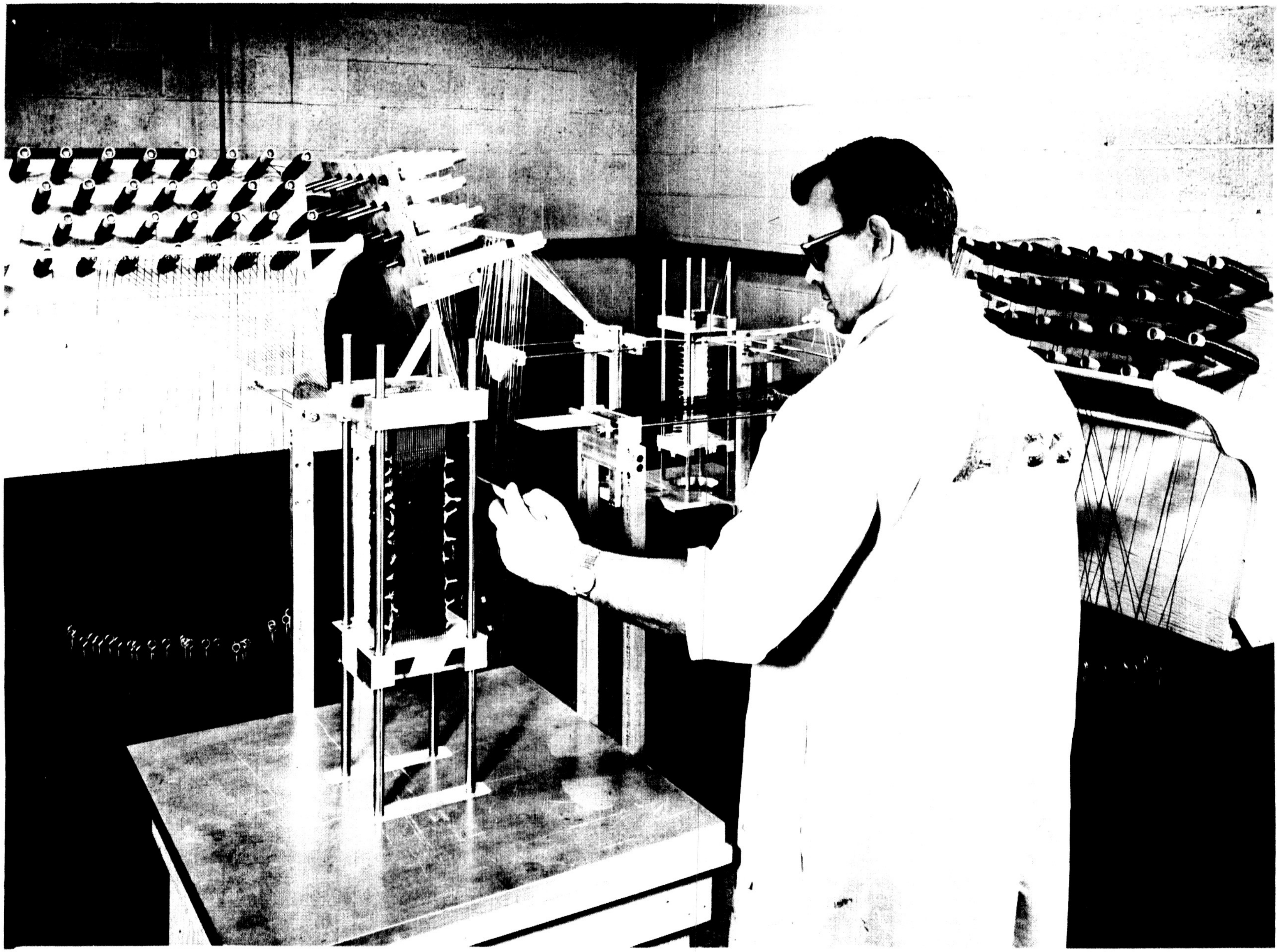


Fig. 3 Avco Loom Unmodified

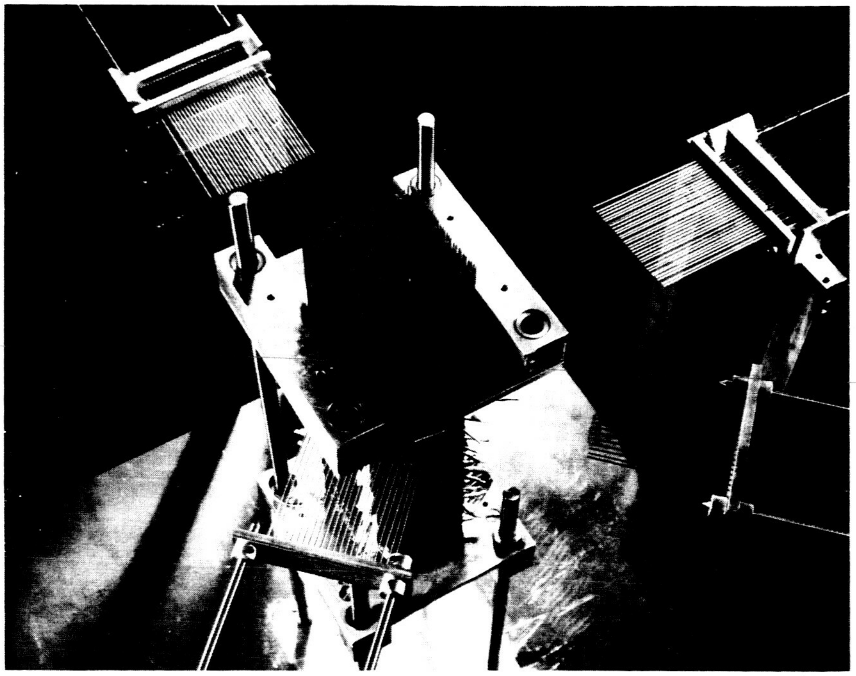
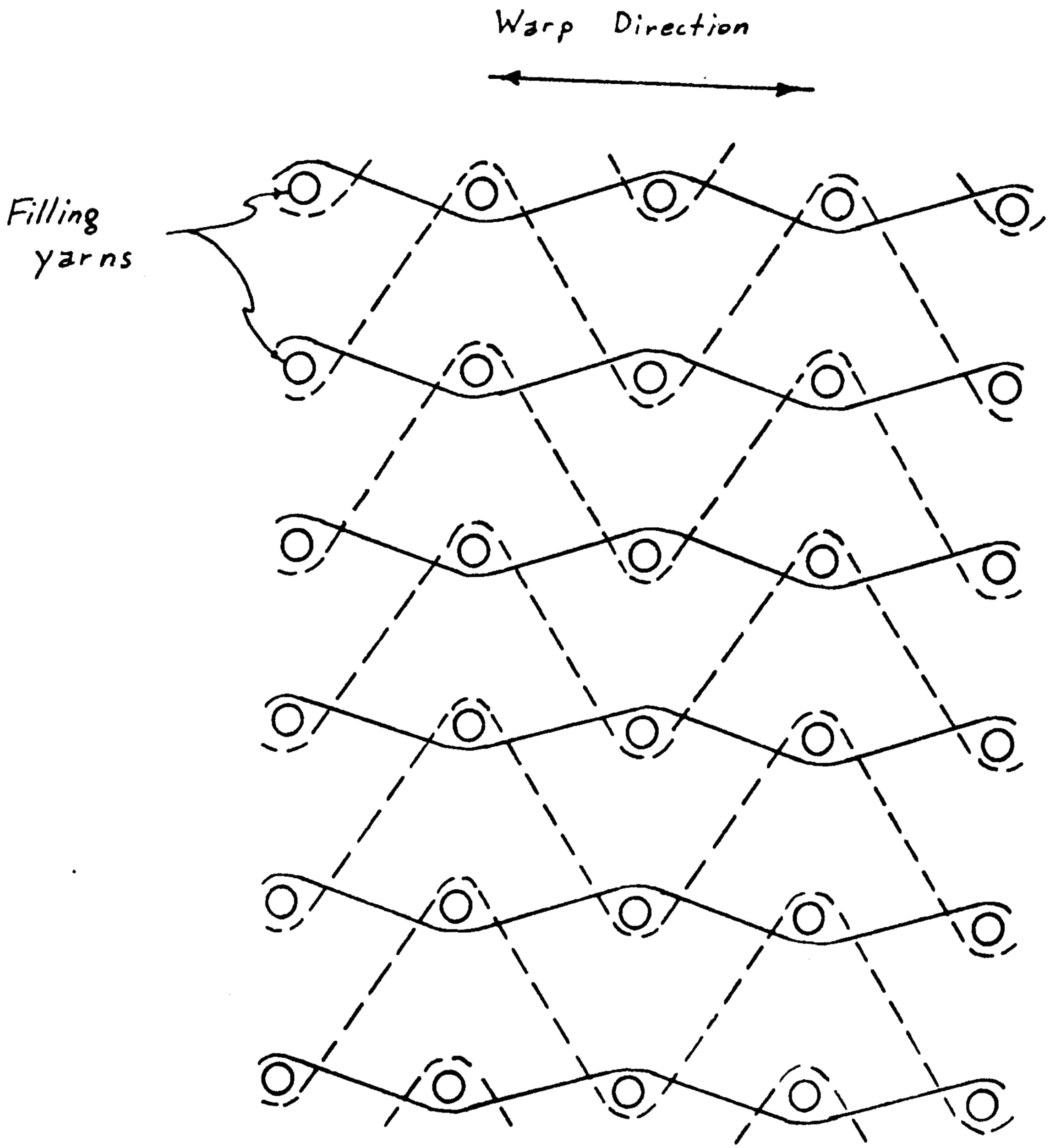


Fig. 4 Avco Loom Modified for 45° Fibers

Figure 5



Six Layers of a
multilayered fabric System

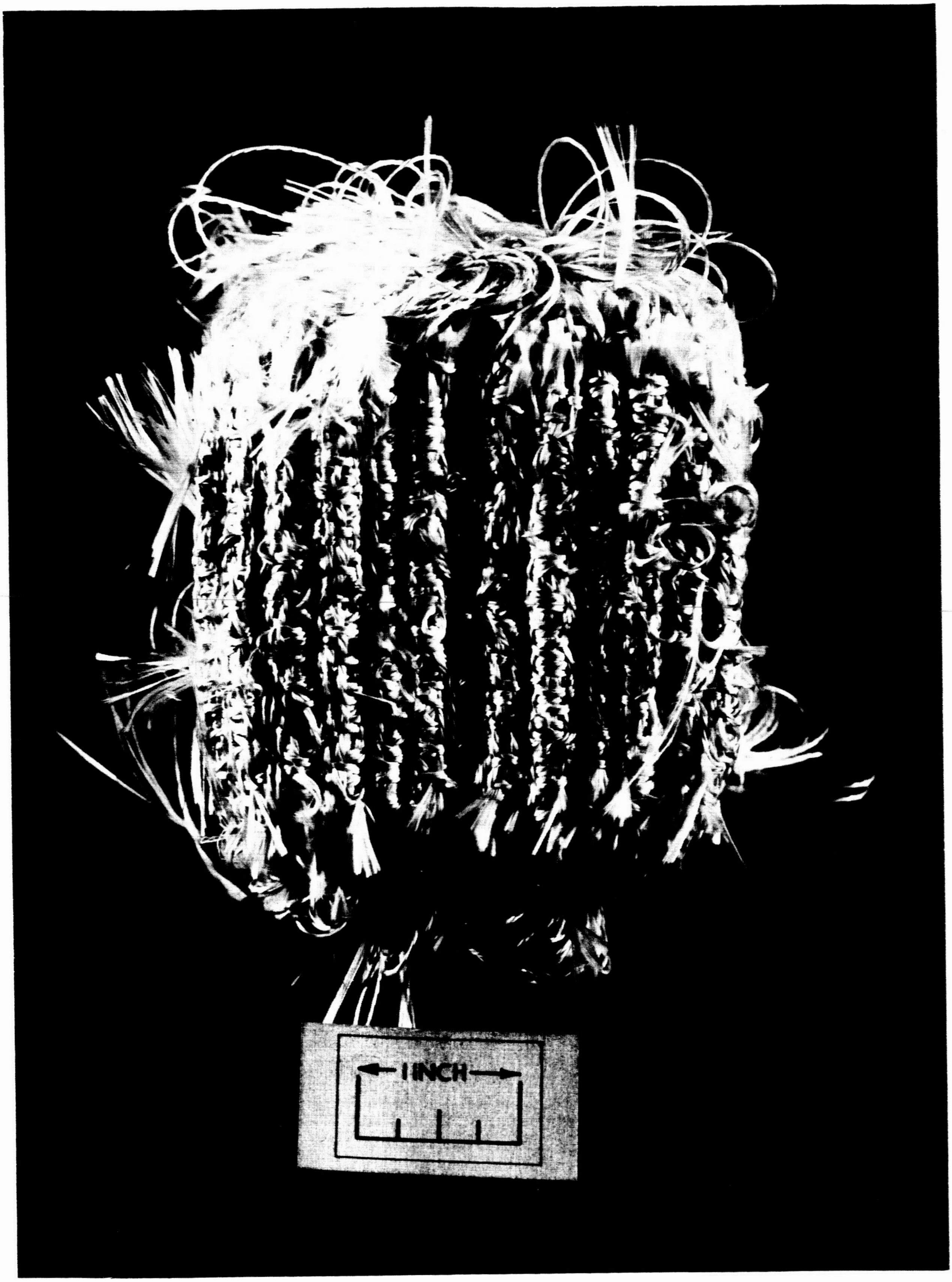


Fig. 6. Raypan Multiple Warp Sewn Fabric Side Wiew

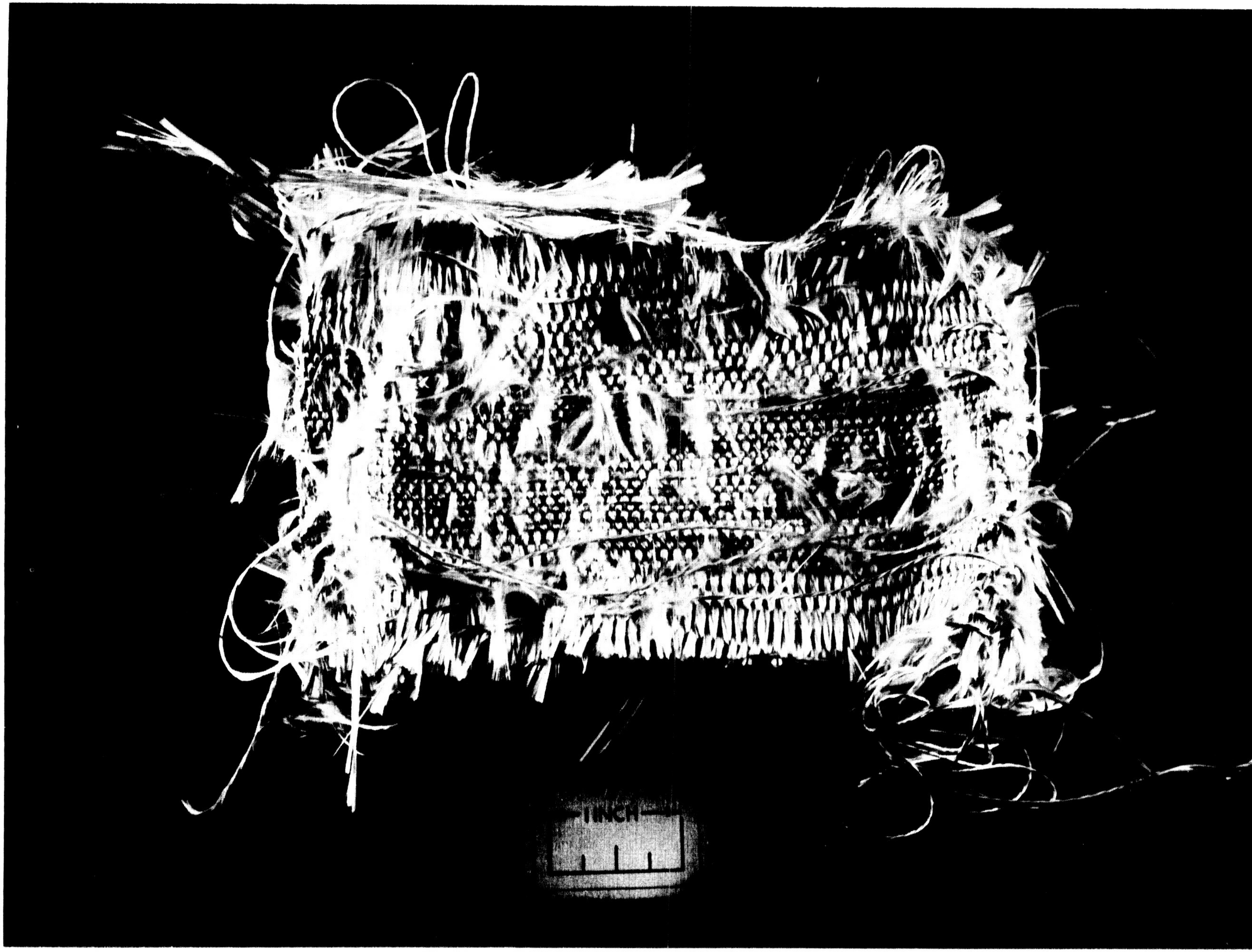


Fig. 7 Raypan Multiple Warp Sewn Fabric Top View

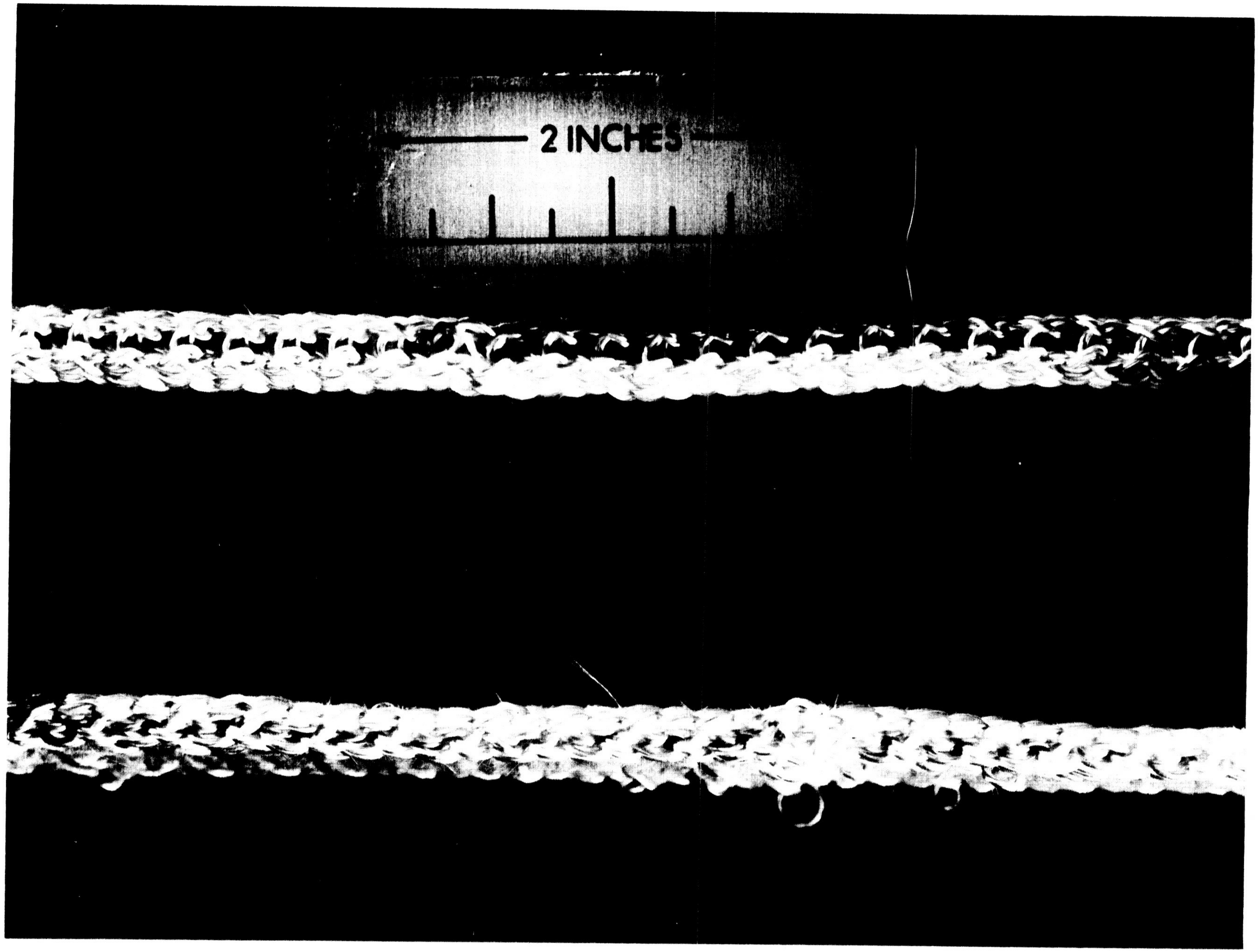


Fig. 8 J.P. Stevens Multiple Warp Side View

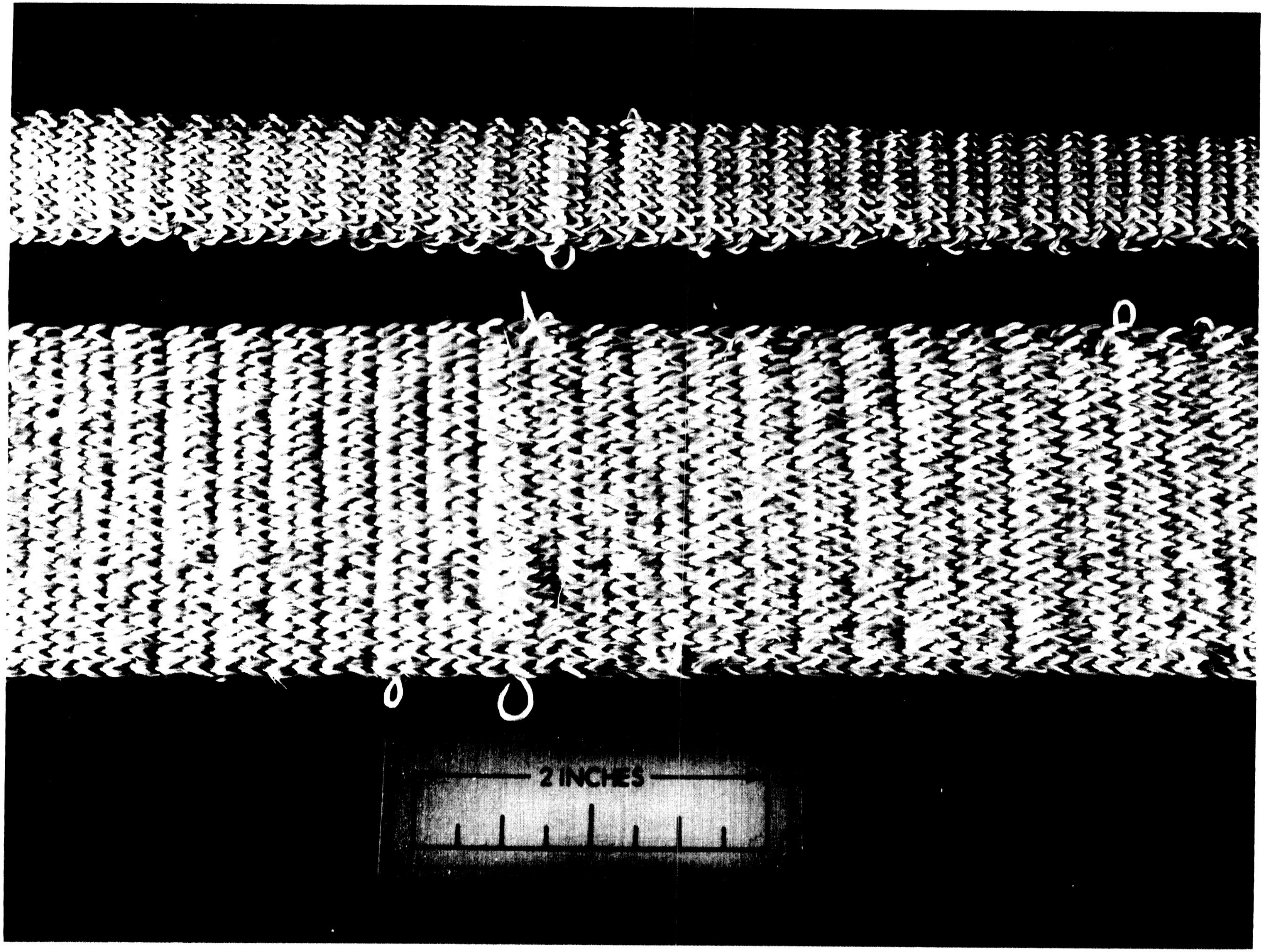


Fig. 9 J.P. Stevens Multiple Warp Top View

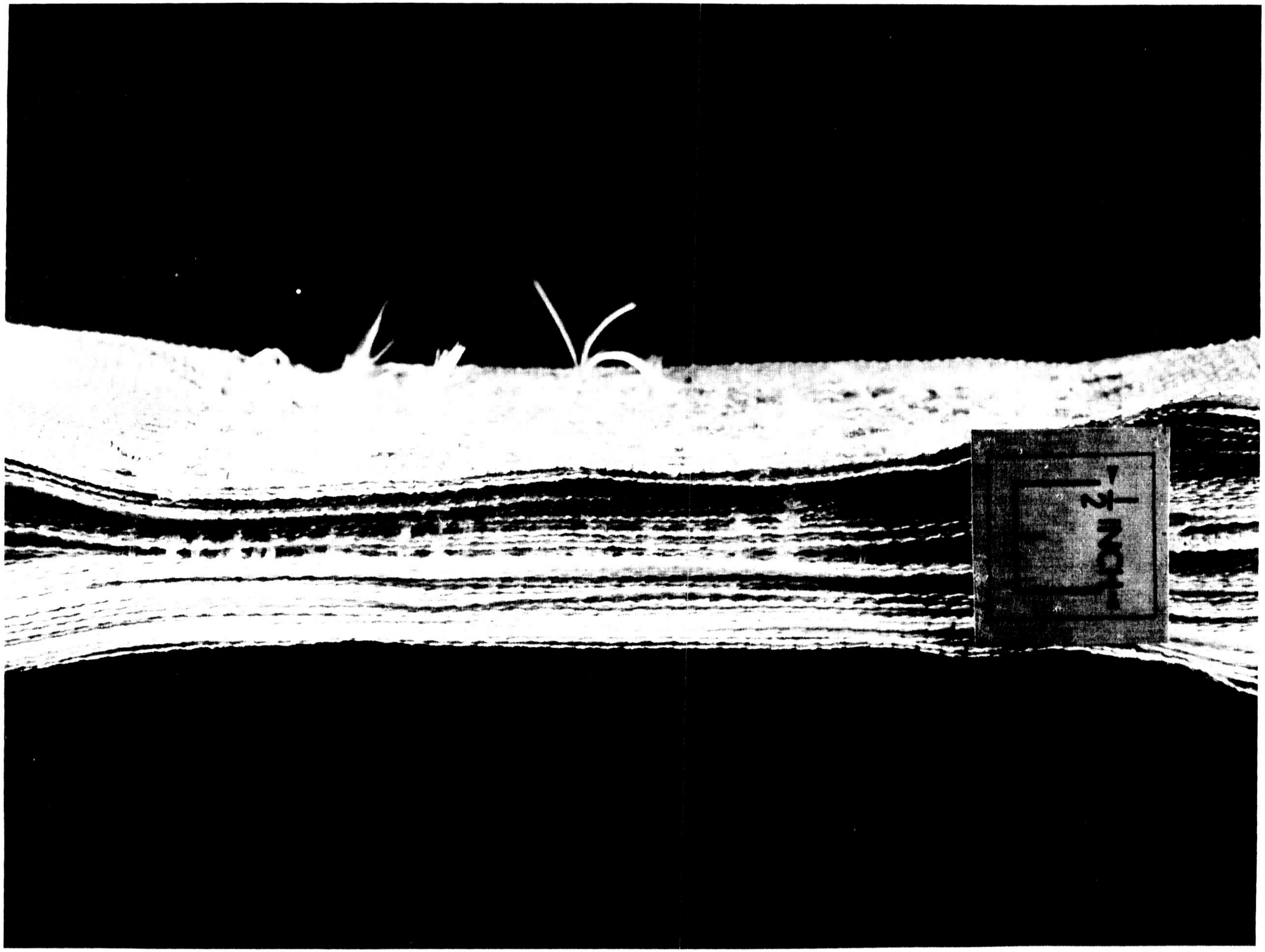


Fig. 10 H.Harwood & Sons Hand Sewn Material Side View

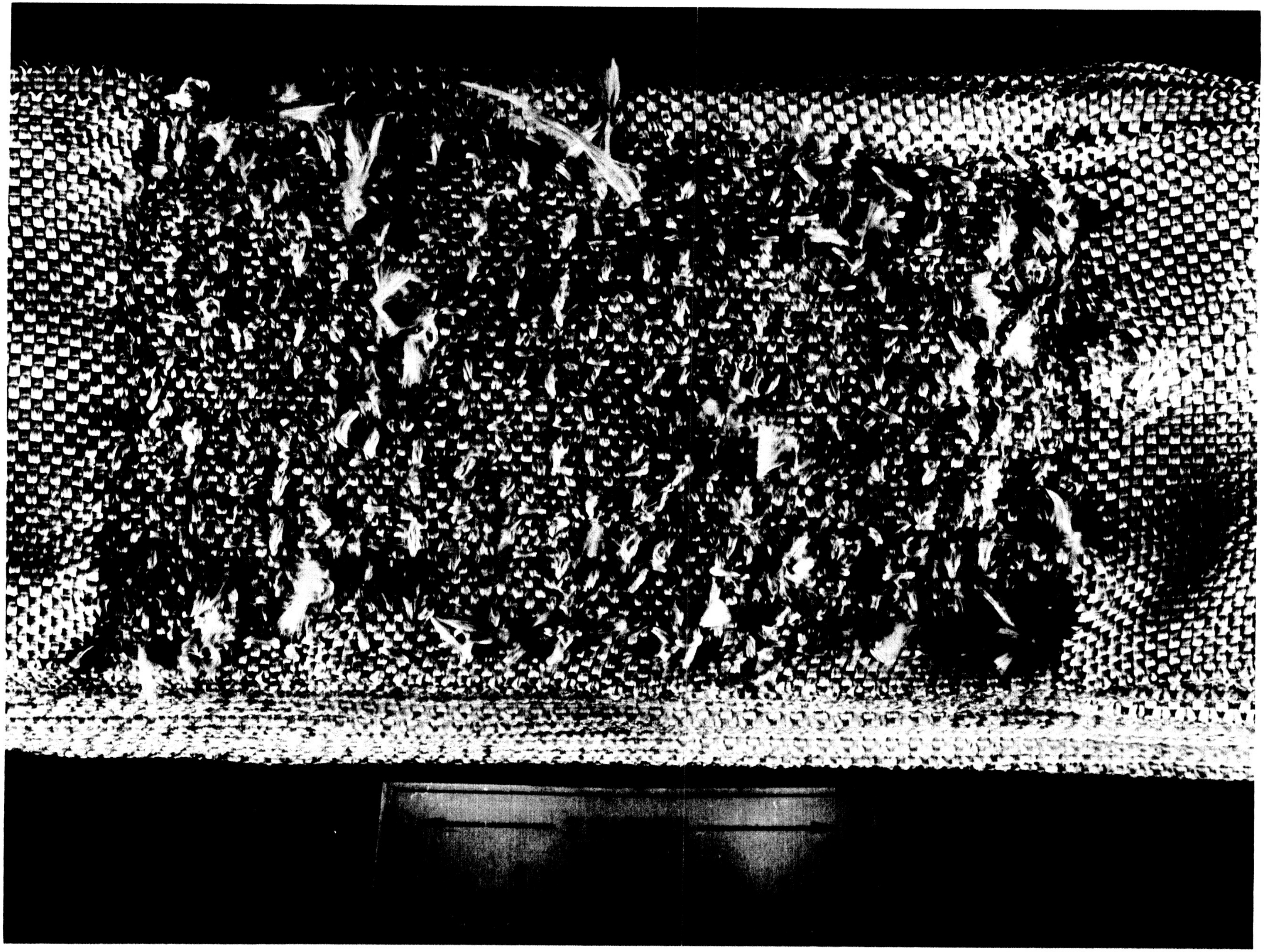


Fig. 11 H. Harwood & Sons Hand Sewn Material Top View

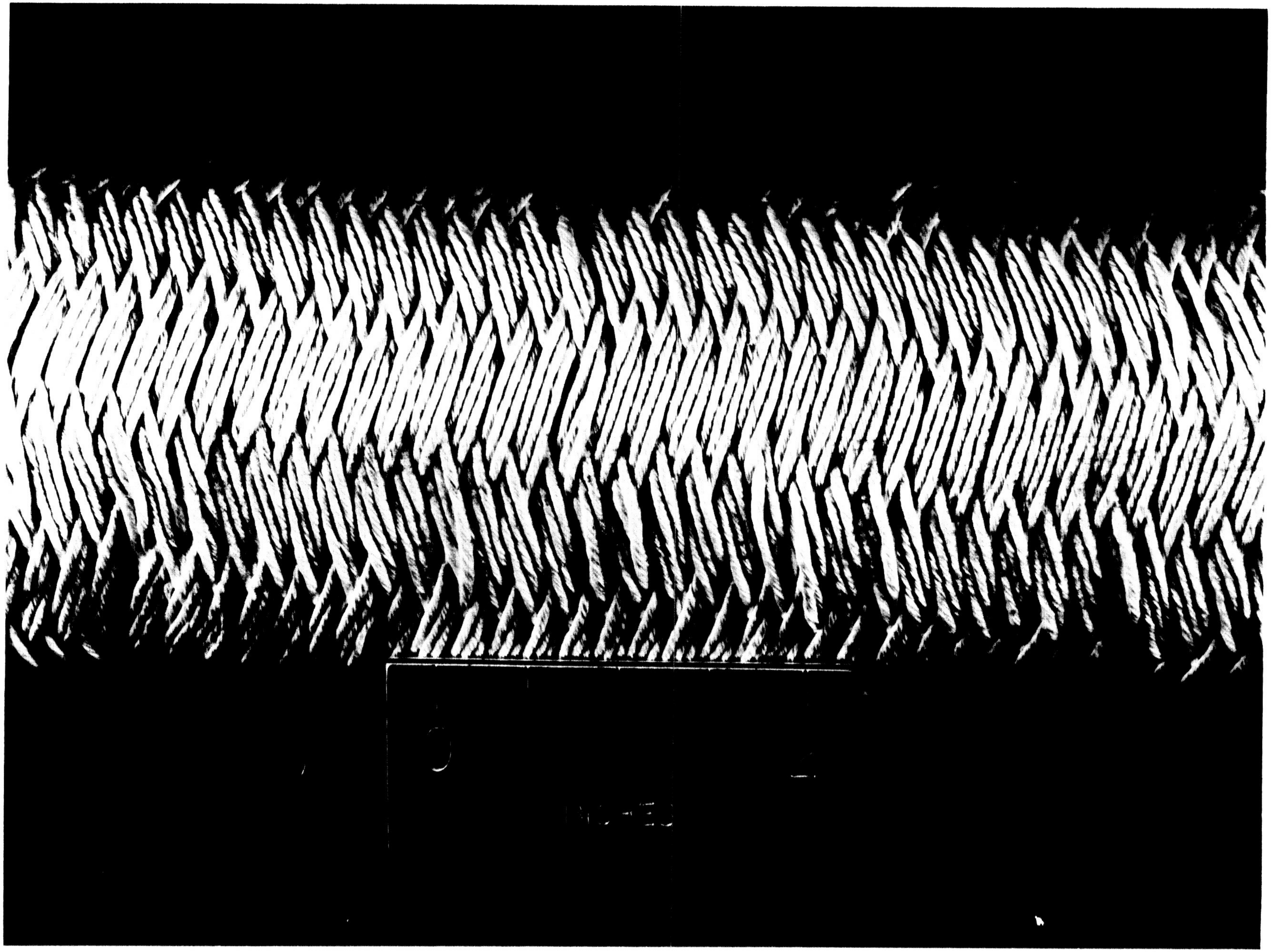
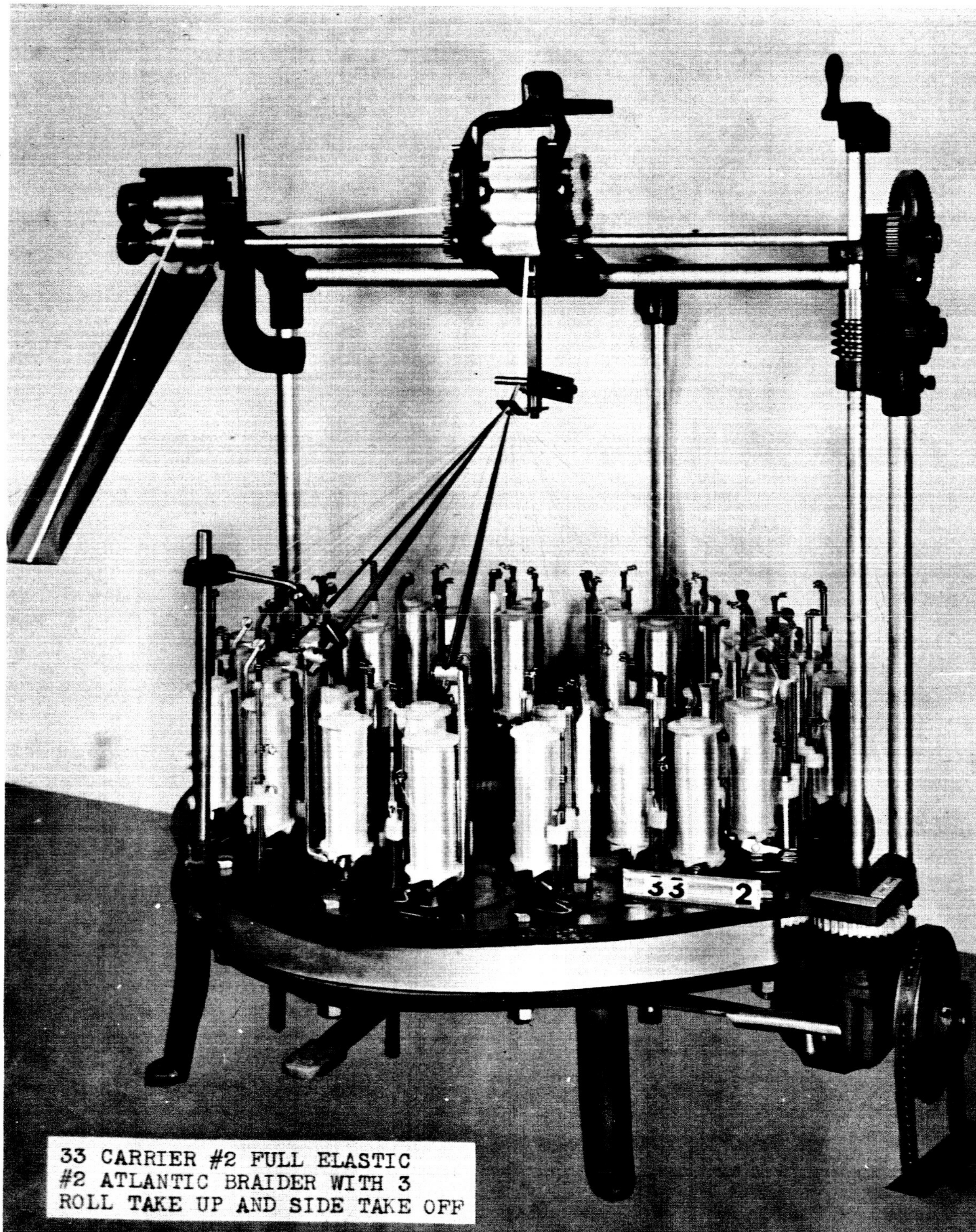


Fig. 12 Valrayco Normal Braid



33 CARRIER #2 FULL ELASTIC
#2 ATLANTIC BRAIDER WITH 3
ROLL TAKE UP AND SIDE TAKE OFF

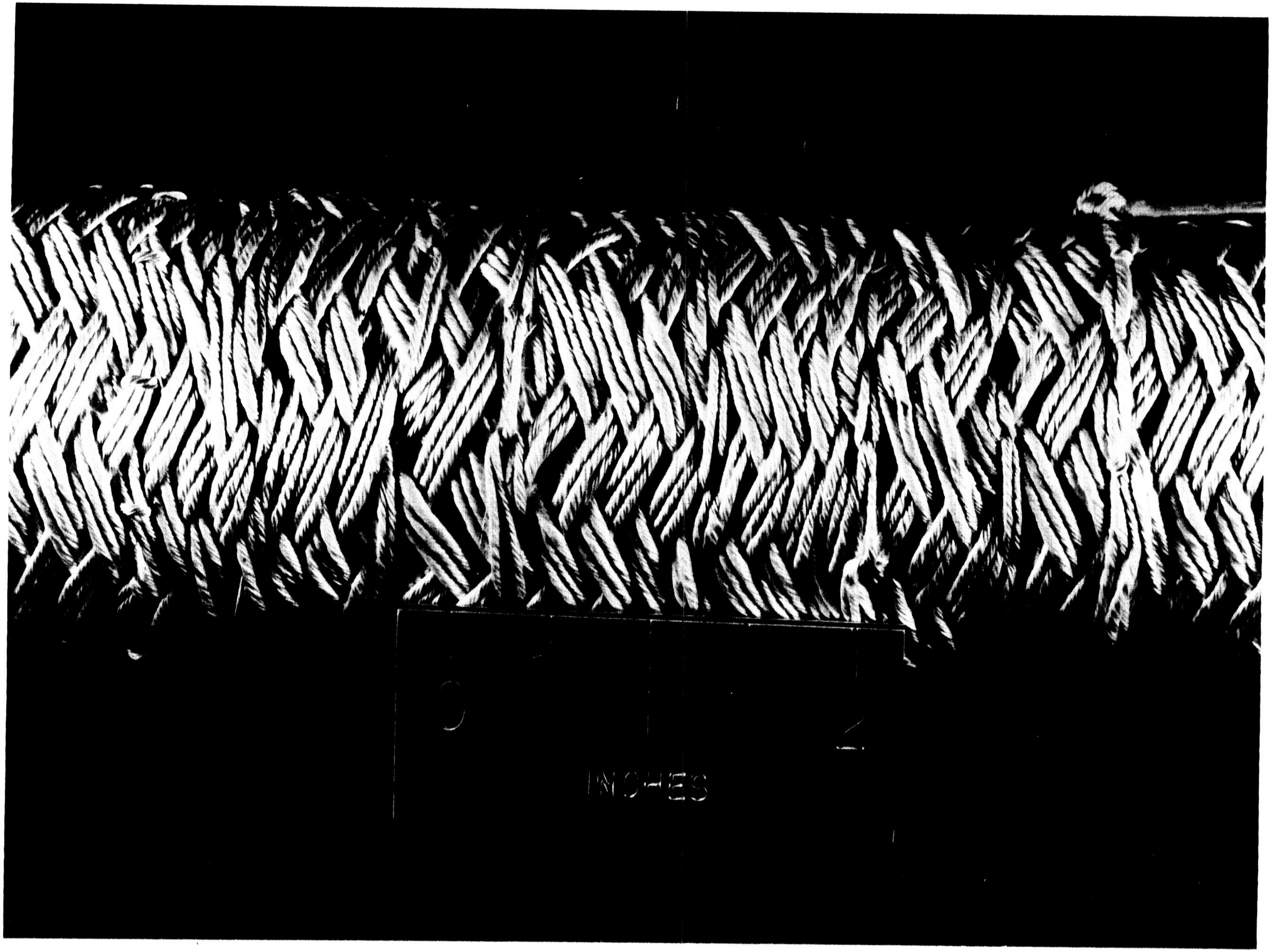


Fig. 14 Valrayco Radially Interlocked Braid

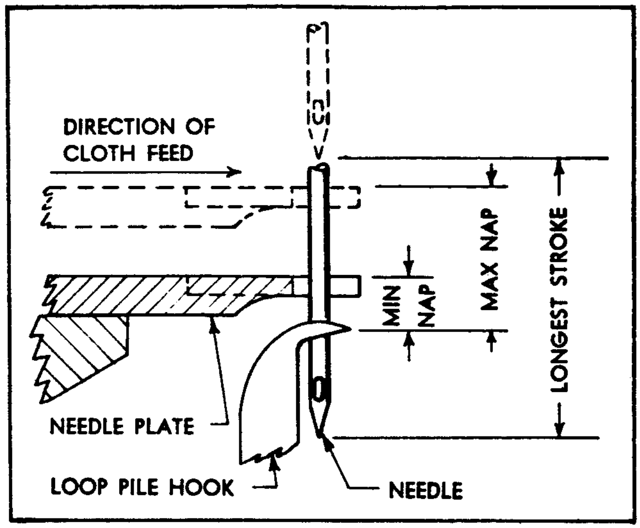


Fig. 15 Diagram of Tufting Mechanism

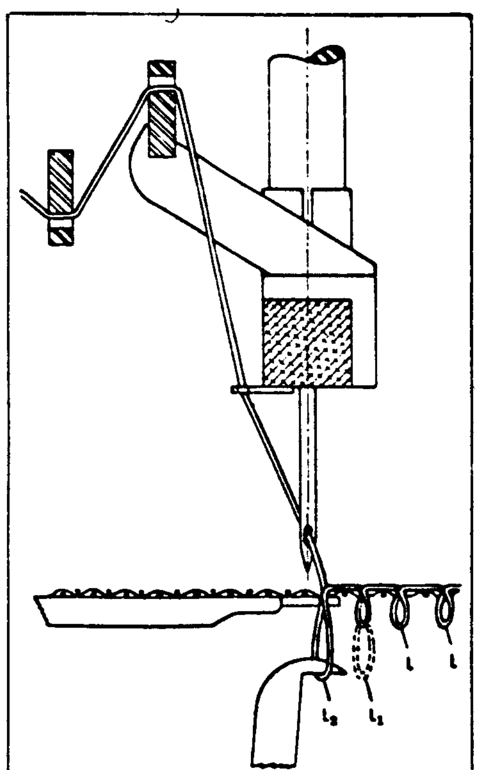
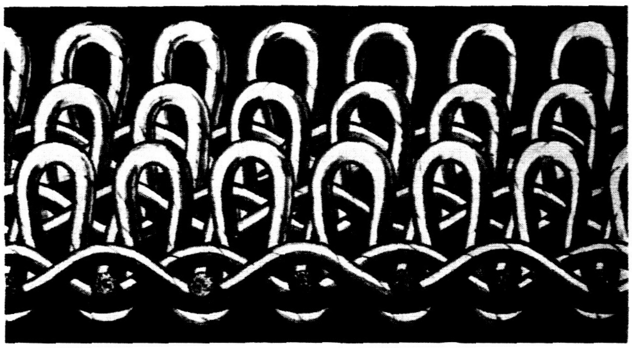
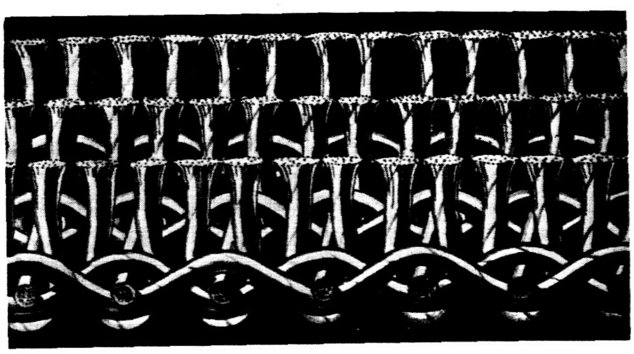


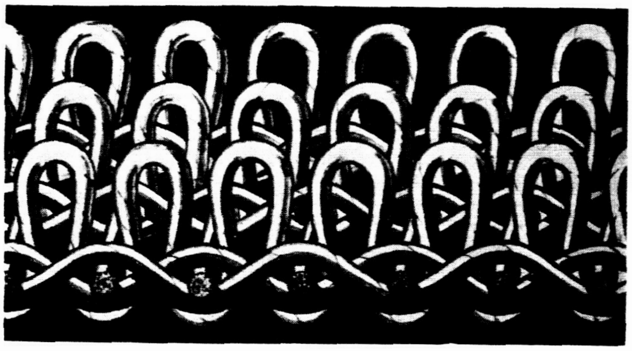
Fig. 16 Diagram of Loop Length Control



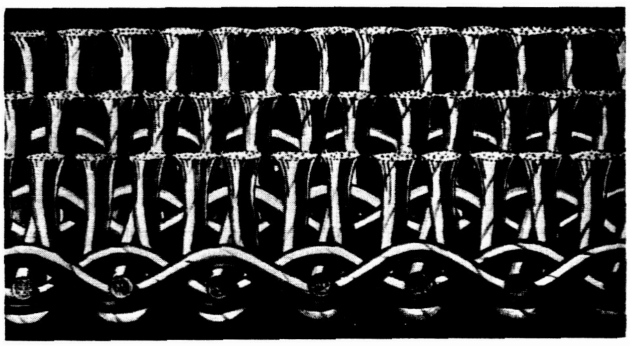
Plain frieze (or uncut pile). This has a surface made up entirely of thousands of tiny, erect loops.



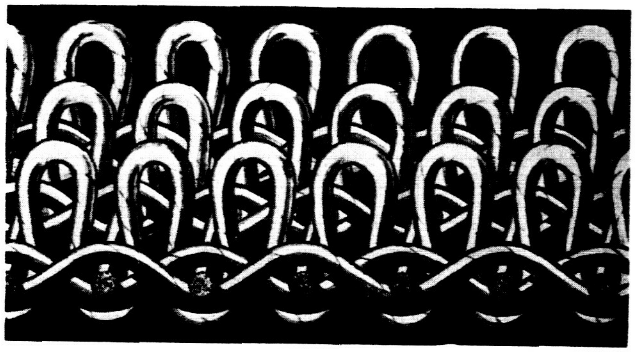
Plain cut pile (velvet). This has a surface or "third dimension" made up entirely of fibers standing on end.



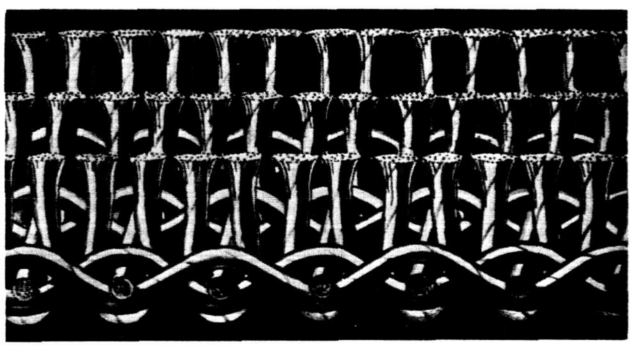
Plain frieze (or uncut pile). This has a surface made up entirely of thousands of tiny, erect loops.



Plain cut pile (velvet). This has a surface or "third dimension" made up entirely of fibers standing on end.



Plain frieze (or uncut pile). This has a surface made up entirely of thousands of tiny, erect loops.



Plain cut pile (velvet). This has a surface or "third dimension" made up entirely of fibers standing on end.

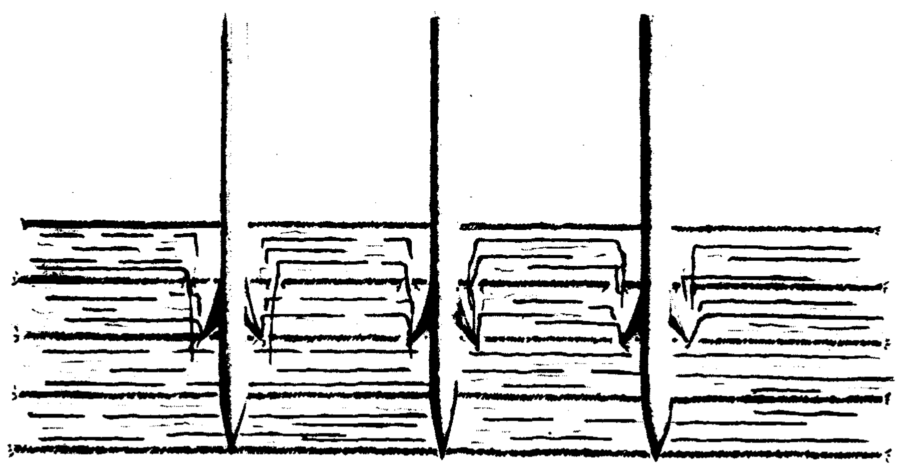
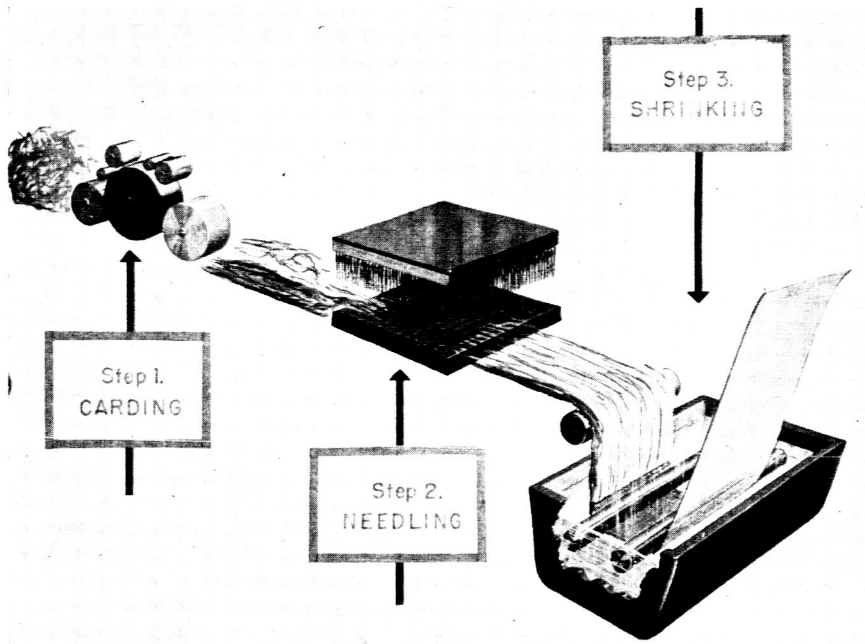


Fig. 19 Diagram of Needling



The three steps in making synthetic fiber felt. (Courtesy *Textile Research Journal*)

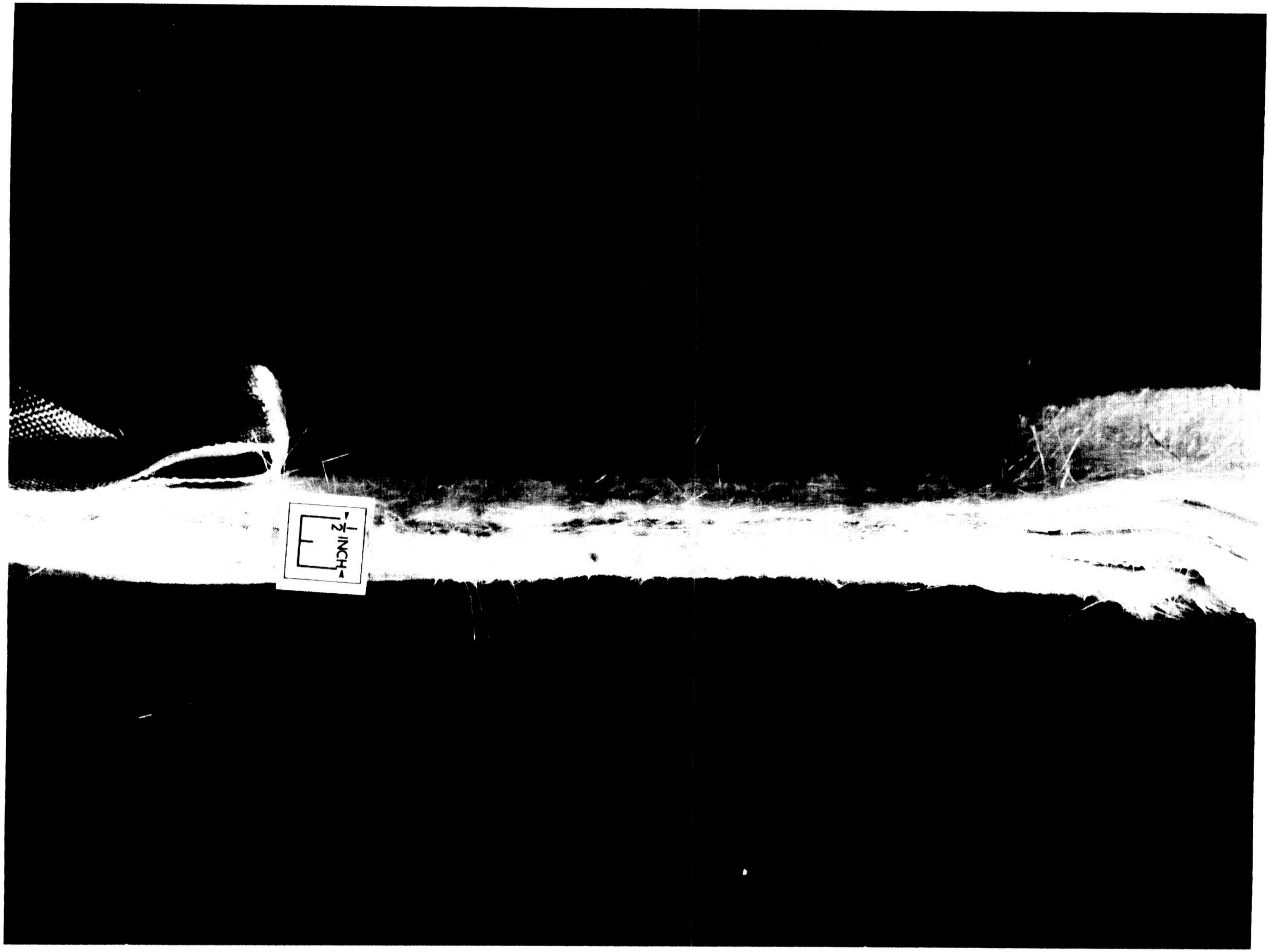


Fig. 21 Needled Matt and Fabric Side View

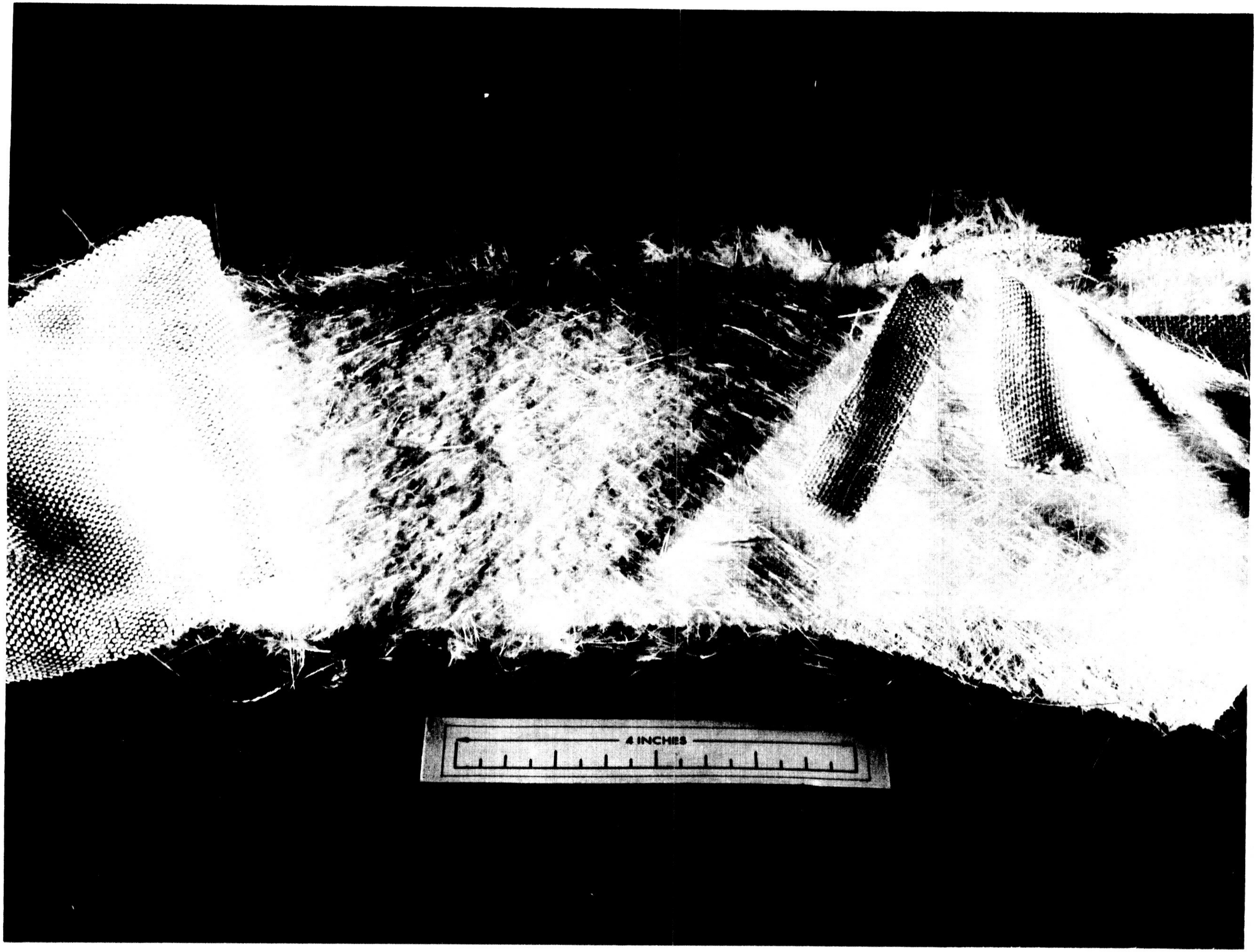
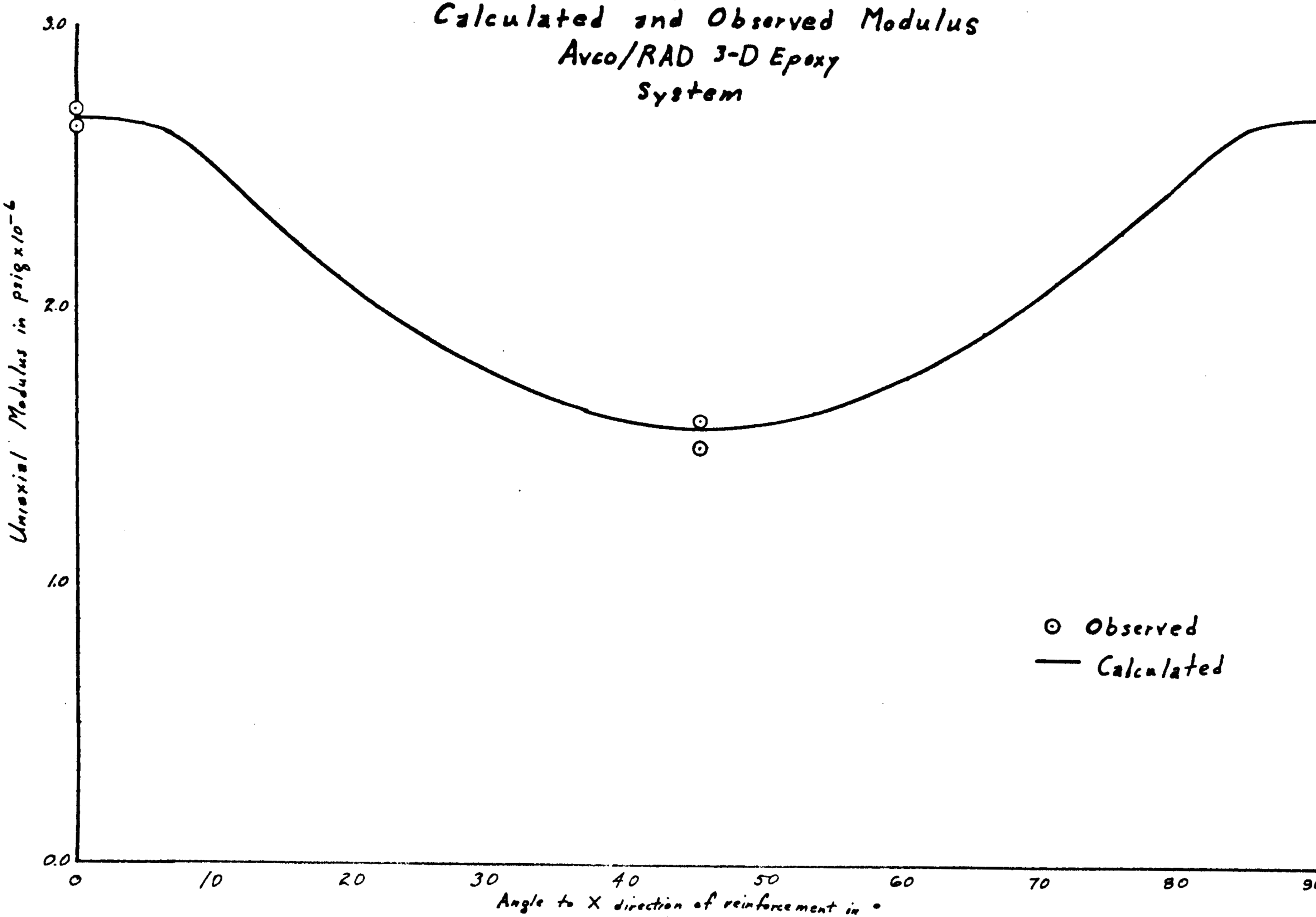


Fig. 22 Needled Matt and Fabric Top View

Figure 23

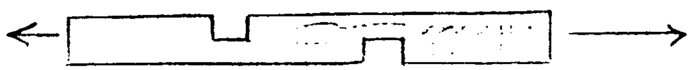
Calculated and Observed Modulus
Avco/RAD 3-D Epoxy
System



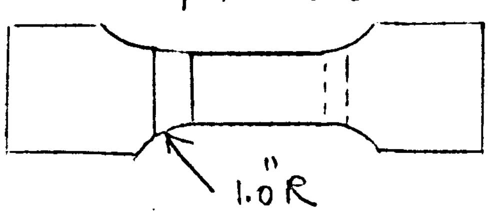
THIN LAMINATES:

NOTCHED SHEAR BAR

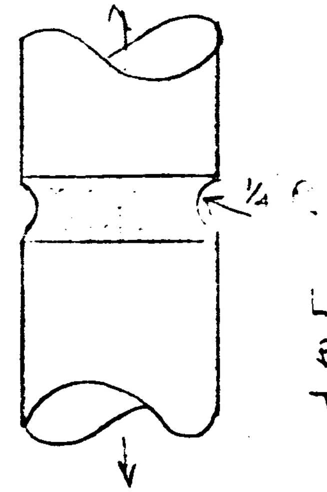
SIDE - VIEW



TOP - VIEW



TAPERED BUTT TENSILE BAR



LAMINATE BONDED TO .75' DIA ALUMINUM RODS

THIN BRAIDED RINGS:

NOTCHED RING SHEAR SAMPLE

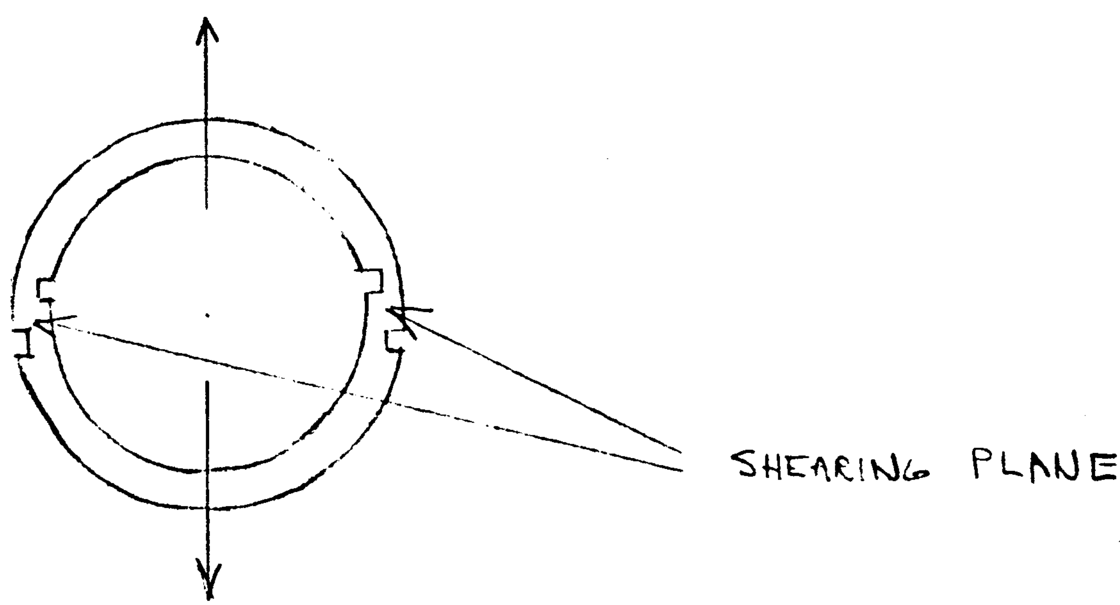


FIGURE 24: SUGGESTED SAMPLE DESIGN

Table I

Results of Phenolic Resin Impregnation Studies

Code No.	Type Reinforcement	Type Resin	Woven or Compacted Density, g/cc	Process Conditions	Density g/cc	Porosity, %	Resin Content, %
874-72 (40)	Avco 3-D	SC1008	1.45	Soaked @ 130°F - Gelled @ 180°F - Press cured 1.4 - Gelled resin to 350°F	1.79	16.0	17.4
874-56	181 Fabric	SC1008	1.51	Soaked & gelled @ 150°F - Press cured to 350°F	1.80	16.0	15.3
874-36	181 Fabric	SC1008	1.50	Soaked & gelled @ 150°F - Press cured in gelled resin to 350°F	1.82	18.4	18.0
874-48 (28)	Avco 3-D	SC1008	1.44	Soaked & gelled @ 150°F - Vacuum bag cured to 350°F	1.76	13.3	15.5
874-40	181 Fabric	SC1008	1.39	Soaked & gelled @ 180°F - Cured in gelled resin to 350°F	1.67	22.8	14.7
874-38	181 Fabric	SC1008	1.41	Soaked @ 180°F - Dried @ 200°F - Cured to 350°F	1.73*	—	21.4*
874-54	181 Fabric	SC1008	1.37	Soaked & gelled @ 180-220°F - Cured to 350°F	1.67	21.3	15.5
874-74 (32)	Avco 3-D	SC1008	1.41	Soaked & gelled @ 150-180°F - Cured to 350°F	1.69	23.5	13.7
874-82	181 Fabric	Colab #397	1.43	Soaked & gelled @ 150-180°F - Cured to 350°F	1.86*	—	23.0*
874-86 (41)	Avco 3-D	SC1008	1.43	Soaked @ 150°F - Dried @ 180°F (3 times) - Cure to 350°F	1.77	14.6	19.4

*Calculated density and resin content values were approximately .03-.05 g/cc and 2.0 to 3.0% higher than expected measured values.

Table II

Comparison of Results of Phenolic and Phenolic/Epoxy Resin Impregnation Studies

Code No.	1st Impregnation - Phenolic			2nd Impregnation - Epoxy		
	Density, g/cc	Porosity, %	Resin Content, %	Density, g/cc	Porosity, %	Resin Content, %
874-72 (40)	1.79	16.0	17.4	1.96	1.0	25.8
874-56	1.80	16.0	15.3	1.81	12.0	16.2
874-36	1.82	18.4	18.0	2.01	0.9	25.1
874-40	1.67	22.8	14.7	1.94	1.1	28.4
874-38	1.73*	——	21.4*	1.95	0.8	27.8
874-54	1.67	21.3	15.5	1.91	1.7	28.3
874-74 (32)	1.69	23.5	13.7	1.92	1.0	26.4
874-82	1.86*	——	23.0*	1.95	1.8	26.6
874-86 (41)	1.77	14.6	19.4	1.91	2.1	26.0

*Calculated density and resin content values were approximately .03 - .05 g/cc and 2.0 to 3.0% higher than expected measured values.

Table III

Avco/RAD 3-D "S" Glass Epoxy System

<u>Tension Tests</u> $75^{\circ}F$, .005 "/"/min = $\dot{\epsilon}$

<u>Vertical Direction</u> (Z axis)

Spec. No.	1	2
Area	143	143
Prop. Limit	2600 psi	1800
Ultimate Tensile Strength	36,000	40,800
Modulus X 10^{-6}	2.67	2.69
Total Strain %	3.6	2.77

Table IV

Avco/RAD 3-D "S" Glass Epoxy System

<u>45° Angle in X-Y Plane</u>

Spec. No.	1	2
Area	.141	.141
Prop Limit	1900	1650
Ultimate Tensile Strength	12,800	12,700
Modulus X 10^{-6}	1.56	1.49
Total Strain %		6.75

Table V

Avco/RAD 3-D "S" Glass Epoxy System

<u>Compression Tests</u> 75°F, = .005 "/"/min.

<u>Vertical Direction (Z axis)</u>

Spec. No.	1	2	3
Area	.109	.110	.110
Prop. Limit	11,200	13,600	14,200
Ultimate Compressive Strength	52,800	59,600	59,100
Modulus X 10^{-6}	1.93	2.0	2.20
Total Strain %	6.54	5.93	6.34

Table VI

Avco/RAD 3-D "S" Glass Epoxy System

<u>Torsion Tests</u> 75°F,

<u>Twist About Vertical Direction (Z axis)</u>

Spec. No.	1	2
Diameter	.377"	.377"
Gage Length	1.0	1.0
Shear Modulus	500,000 psi	571,000
Ultimate Shear Strength	10,100	14,500
Total Twist in Degrees	130°	130°

Table VII

Avco/RAD 3-D "S" Glass Epoxy Resin

<u>Twist About 45° Direction in X-Y Plane</u>

Spec No.	1	2
Diameter	.379	.379
Gage Length	1.0	1.0
Shear Modulus	800,000	615,000
Ultimate Shear Strength	10,700	10,000
Total Twist in Degrees	190°	185°

Resin Content - one sample for 3/8" dia. x 1/2" long - 22.5%*

* This value may be low

Table VIII

Raypan 3-D Epoxy System

Tension Tests at 75^{o}F, .005 "/"/min.

Parallel to Laminates

Spec. No.	1	2	3	4	5	6	7	8	9	10
Area	.039	.039	.039	.039	.039	.039	.039	.039	.039	.039
Prop. Limit	1400	3600	4400	2750	2750	3000	4000	4500	1750	4250
Ultimate Tensile Strength	6600	14,000	19,300	17,300	23,700	23,600	16,500	20,100	9350	19,000
Modulus X 10^{-6}	2.55	2.91	3.65	3.35	3.52	3.52	3.54	3.35	3.24	3.07
% Total Strain	.48	.68	.78	.74	1.52	1.40	.66	.82	.52	1.29

Table IX

Raypan 3-D Epoxy System

Torsion Tests $75^{\circ}F$

About Axis Perpendicular to "Laminations"

Spec. No.	1	2	3	4
Diameter	.314	.310	.313	.310
Gage Length	1.0	1.0	1.0	1.0
Modulus	471,000 psi	533,000	533,000	471,000
Ultimate Shear Strength	6700 psi	6320	5880	5910
Total Twist in Degrees	12°	10°	9°	10°

Table X

Raypan 3-D Epoxy System

Resin Content

Specimen No.	% Resin
1	23.
2	30.5
3	24.75
4	24.6
5	27.4
6	24.1
7	25.6
8	26.
9	24.7
10	28.3